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The Application of Soluble Oils in the Processing of Textiles*

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THE major outlets for oils in the textile industry may be divided into three general classifications: first, in the preparation of yarn to improve its weaving, knitting or finishing qualities; second, in scouring, dyeing and printing to insure wetting, penetration and levelness; and third, for finishing the cloth to produce the desired appearance and feel and, consequently, improve the "merchandisability" of the fabric.

I shall limit the subject of this paper to a general discussion of the various uses for oils and fats in the processing of cotton and rayon, and especially to their application in the finishing of cloth composed of these fibers. I shall attempt to show how the chemical and physical characteristics of oils determines their fitness or unfitness for the processes in which they may be applied.

Regardless of which of these three uses the oils are to be put, it is the general practice to apply them to the yarn or cloth in an aqueous medium. These oils must, therefore, possess the property of dispersing readily in water. The best way to prepare oils intended for textile use, so that they will be miscible with water and still retain many of the desired "oily" properties, is to treat them with sulfuric acid, thereby forming sulfo-compounds which are usually soluble in water in all proportions. Many of these sulfonated oils have the property of being able to carry varying amounts of raw oil, either saponifiable or mineral, into emulsion with themselves. This type of compounded oil has found extensive use in the preparation of yarn for knitting and weaving, and also in the finishing of cloth.

Due to the fact that practically all processing oils used in the textile industry consist of either sulfonated oils or mixtures of sulfonated and raw oils, I would like to briefly touch upon the manufacture of this type of modified oil and to mention some of its important characteristics.

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†The United States Finishing Company. Member: Committee on Analysis and Grading of Sulfonated Oils, American Oil Chemists Society. Committee on Analysis and Grading of Sulfonated Oils, American Association of Textile Chemists and Colorists.

The past several years have witnessed an increasing demand upon the sulfonated oil manufacturer for products of superior qualities, such as oils which are resistant to the action of magnesium and calcium salts, acids, alkalies, and other strong electrolytes; oils which are proof against oxidation and the subsequent development of discolorations and objectionable odors; oils which will have no appreciable effect upon the shades of some of the more sensitive dyestuffs; and there are many other specifications which these sulfonated oils are now called upon to meet. As a result of these demands, the manufacturer has developed oils which now meet every condition imposed upon them by the industry. These new developments have emphasized the need for uniform and standard methods for the analysis and grading of sulfonated oils. I might mention at this time that a study is now being made by a committee appointed by your society which is working in conjunction with a similar committee of the American Association of Textile Chemists and Colorists with the object of standardizing methods of analysis and grading of sulfonated oils.*

SULFONATION PROCESS

If each saponifiable oil consisted of a single organic compound, or if they always contained the same mixture of compounds in the same proportion, or if the reaction between sulfuric acid and these oils proceeded in regular fashion along one line, then the manufacture of sulfonated oils would be greatly simplified. The unfortunate part is that naturally occurring oils do not possess these properties and, consequently, the sulfonator is faced with

*Reports of these committees: Oil and Soap, Vol. XI, No. 11, p. 229 (1934). American Dyestuff Reporter, Vol. XXI, No. 24, p. 667 (1932). Ibid., Vol. XXII, No. 24, p. 695 (1933). Ibid., Vol. XXIII, No. 11, p. 290 (1934).

innumerable side reactions in his process with which he must cope.

The sulfonation process usually consists of three steps: first, sulfonation; second, washing; and third, neutralization. When concentrated sulfuric acid is allowed to react with a saponifiable oil under definitely controlled conditions, there are formed the sulfuric esters of the unsaturated glycerides and fatty acids contained in the oil. The sulfuric acid attaches itself to the fat molecule in this case through an oxygen linkage. Under certain conditions, it is possible to form, in varying amounts, the true sulfonates in which the sulfuric radical is attached directly to the carbon atom. These two reaction-products may be varied between certain limits at the will of the manufacturer. There are also several other reactions, usually undesirable, which generally occur during sulfonation, such as the formation of lactides and other polymers. Also, a certain amount of hydrolysis takes place setting free small amounts of glycerine and fatty acids.

The second step in the sulfonation process consists in removing the uncombined sulfuric acid and other soluble impurities. This may be accomplished by treating the sulfonated oil with water or with an aqueous solution of sodium chloride, sodium sulfate, or other similar electrolyte. The mixture is allowed to settle for some time, during which it will resolve itself into two distinct layers, —a lower aqueous layer which will contain most of the free sulfuric acid with other soluble organic impurities from the oil, and an upper layer which will contain the sodium salts of the fatty acid-sulfuric esters, free fatty acids, neutral uncombined oil, and the various polymerization products formed during the process. Many reactions may occur during the washing process, depending entirely upon the method employed in this operation. In almost all cases, however, considerable hydrolysis takes place with consequent liberation of glycerine and fatty acids. This sometimes occurs to such an extent that the final product may contain no combined glycerine whatever. On the other hand, this reaction may be so controlled that there is practically no hydrolysis of the glycerides at all. Another undesirable hydrolysis that sometimes takes place during this period is the splitting off of sulfuric acid from the sulfuric ester, with consequent loss of organically combined sulfur trioxide.

The third step in the process consists of adjusting the oil with alkali to the proper pH, depending upon the use for which the oil is intended. At this point all traces of mineral acid are completely neutralized; a certain amount of the free fatty acids present are also neutralized and in some instances sufficient alkali is added to completely neutralize all of the free fatty acids and to saponify a part or all of the neutral fat.

The resulting sulfonated oil may contain from 0.5 percent to 20.0 percent of organically combined sulfur trioxide, from 5.0 percent to 90.0 percent of free fatty acids, and from 0.5 percent to 9.0 percent of combined alkali (Na_2O). As may be seen, these constituents can be varied between rather wide limits. They all have a definite bearing on the use of the sulfonated oil in the textile plant.

PREPARATION OF YARN

To refer back to the three classifications into which the application of sulfonated oils may fall, the first is in the preparation of yarns before knitting or weaving. Yarn which is intended for knitting is treated with oil to soften and lubricate it so that it will run smoothly, with minimum breakage, in the knitting machine. The oiled yarn also serves to lubricate the knitting needles and prevent them from overheating.

In the preparation of warp yarn for weaving, it is run through a preparation of size, which for cotton generally consists of a mixture of gum or starch with a sulfonated or emulsified oil, whereas for rayon a mixture of gelatin or casein with sulfonated oil is usually used. This sizing serves two purposes: first, it imparts to the yarn a certain resistance to abrasion, thereby protecting it from the friction of the rapidly moving shuttle in the weaving loom; and secondly, it affords lubrication and pliability to the yarn, allowing it to be flexed repeatedly in opposite directions while in the loom, with a minimum of breakage.

In the manufacture of rayon crepes, it has been found quite essential to treat the filling yarns with so-called soaking oils before weaving them into the fabric. This pre-treatment tends to produce a superior "pebble" or crepe effect to the finished cloth which cannot be obtained with crepes constructed from unoiled yarns. These soaking oils are generally used in conjunction with glue or gelatin, which in turn help to produce certain desirable characteristics in the finished fabric.

Oils which are used in these oiling, sizing and soaking operations do not come in contact with electrolytes of any type and, consequently, are not required to be highly sulfonated. The color and odor are not of great importance as the oil is subsequently removed from the fabric in the finishing plant. Oils for these uses, however, must possess the proper penetrating power and lubricating properties essential to the attainment of the desired result. They must also be in such form that they may be readily removed from the fabric in the finishing operations so that they will not interfere with any of the bleaching, dyeing or printing processes.

The numerous oils which are now being marketed for the aforementioned purposes vary widely in their composition. The following is suggestive of the types being used:

A. Knitting Oils

1. Sulfonated Olive Oil.
2. Sulfonated Olive and Coconut Oil Mixtures.
3. Compounded Oils.*

*Oils consisting of mineral oil and an emulsifier such as sulfonated oil, soap or naphthene sulfonates.

B. Warp Sizing Oils

1. Sulfonated Tallow.
2. Sulfonated Castor Oil.
3. Sulfonated Olive Oil.
4. Emulsified Tallow.
5. Emulsified Coconut Oil.
6. Compounded Oils.

C. Rayon Soaking Oils

1. Sulfonated Tallow.
2. Sulfonated Castor Oil.
3. Sulfonated Olive Oil.
4. Sulfonated Olive and Coconut Oil Mixtures.
5. Compounded Oils.

SCOURING, DYEING AND PRINTING

The second major use for sulfonated oils in the textile field lies in their value as scouring, dyeing, and printing assistants. In scouring operations we find that certain types of sulfonated oils may be added to the bath with definitely improved results. This is especially true when the oils are compounded with a good solvent such as pine oil, cresylic acid, xylol, tetralin, etc. Oils of this type owe their usefulness to their surface active properties, i. e., to their power of reducing the interfacial tension between the scouring solution and the fiber. Satisfactory results cannot be expected from scouring agents which do not possess the property of wetting the surface of the fiber readily and completely. An otherwise poor scouring agent may sometimes be rendered very efficient by the addition of a small amount of a suitable penetrant or wetting agent.

The preliminary scouring or "kier boiling" of cotton cloth preparatory to bleaching is generally conducted in closed vessels under a steam pressure of approximately fifteen pounds per square inch. The scouring solution is continually circulated through the cloth for a period of ten to fourteen hours. In this operation the addition of a penetrant does not always show to advantage due to the time and pressure factors, which allow maximum contact and penetration of the scouring bath without the aid of assistants.

However, in the scouring of rayon and acetate silk, where the operation is conducted in an open bath under atmospheric pressure, the use of penetrant oils has been found of considerable advantage. Here the scouring agent usually consists of soap, with or without the addition of alkali. The length of time required in scouring these types of fabric varies from ten minutes to two hours. With this limited time factor to contend with, the use of penetrants usually shows up to a decided advantage by bringing the scouring bath into intimate contact with the cloth fibers during the first few minutes of immersion.

Oils intended as scouring assistants must be capable of lowering interfacial tensions of alkaline aqueous solutions to a marked degree; they must be sufficiently stable to stand plant operating conditions without separating any oil or solvent; and in some cases they must be somewhat resistant to the action of calcium salts in the water. Color, odor and oxidizing tendency are not of prime importance.

After the cloth has been scoured and bleached, it is ready for the dyehouse or print room where we find further applications for sulfonated oils. In the dyebath the sulfonated oil may serve three distinct purposes. It may act as a solvent or dispersing agent for the dyestuff. It may act as a penetrant, thus helping the color to get to the center of the fiber. The most important property of a sulfonated oil as it relates to the dyeing process, however, depends upon its colloidal properties in aqueous solution. This property allows it to retard the rate of adsorption of dyestuff on the cloth. In performing this function it aids considerably in the production of bright, even shades, free from streaks, blotches and cloudiness. In the dyeing of so-called "mordant" colors, it is stated that sulfonated oils, especially sulfonated castor oil, actually enter into chemical combination with the precipitated color producing brighter and faster shades.

The dyebath often contains moderate concentrations of electrolytes, such as sodium chloride, sodium sulfate, acetic acid, formic acid, etc. Dyeing oils consequently must be resistant to the effect of electrolytes of these types. They must also possess the required colloidal properties in solution which will make them of value in the dyeing process. The mechanism of dyeing is not fully understood and little is known of the exact function of the sulfonated oil in this process. However, the effects of sulfonated oils in the dyebath are fully realized and it is known that certain types of oil are better adapted for this use than others. Again, it is not essential that dyeing oils be of good color, odor, or free from oxidizing tendencies.

In the printing of designs on cotton or rayon cloth, the essentials of good work are: first, that the color be in the proper state of solution or sub-division; second, that the color be so combined in the printing paste that it does not string or spread on the cloth as it leaves the engraved roller; third, that it wets the cloth quickly and completely and penetrates the fiber. The use of sulfonated oils helps to improve all three of these properties in a print paste. It serves in the first place to aid in the solution or dispersion of the dyestuff itself, and in so doing goes a long way in helping to eliminate dye specks or streaks on the cloth. Certain oils, especially compounded oils, help to produce smoothness and uniformity in a print paste, resulting in a better running mixture with little tendency to string or dry out on the surface. In this respect the oil also acts as a lubricant between the doctor blade* and the engraved roller, and prevents accumulation of dried scum between the two, with subsequent specks and streaks appearing on the printed cloth. The sulfonated oil also serves the purpose of a wetting agent

*A spring steel blade which rests against the engraved printing roller and serves to remove the excess color from the smooth surface of the roll.

and allows the color to wet and penetrate the cloth readily. This last result is obtained either by incorporating the sulfonated oil in the print paste or by treating the entire cloth with a solution of the oil and drying it in before printing.

Printing oils do not need to be especially stable, as they are generally incorporated in the print paste with gums and starches, and there is little possibility of separation. As previously stated, it is often of advantage to use compounded oils in printing. Other requirements for good printing oils are that they possess the desired surface active properties to insure efficient wetting and penetration of the fiber, and also that they be good dispersing agents for the dyestuffs with which they are used. Odor, color and tendency to oxidize are again of minor importance.

The following list will afford some idea of the variety of oils which are being used in scouring, dyeing and printing operations:

A. Scouring Oils

1. Sulfonated Castor Oil.
2. Sulfonated Red Oil.
3. Penetrant Oils*.

B. Dyeing Oils

1. Highly Sulfonated Castor Oil.
2. Highly Sulfonated Olive Oil.
3. Penetrant Oils.

C. Printing Oils

1. Sulfonated Castor Oil.
2. Sulfonated Red Oil.
3. Compounded Oils.
4. Penetrant Oils.

FINISHING

We now come to what is by far the greatest outlet for sulfonated oils in the textile industry, that is, in the actual finishing of cloth. This is the last wet operation to which the cloth is subjected previous to its appearance on the market. Here are added to the cloth substances which enhance its appearance and feel, thereby increasing its "salability". Sulfonated oils or emulsified oils and waxes used for finishing are usually termed "softeners", although they are not always added to the cloth to impart that property. Softeners play a major role in the finishing process because, by their use, the finished appearance of a fabric may be varied between wide limits. The desired finish depends upon the type of cloth and the use for which the cloth is intended. Some fabrics require a maximum stiffness, others require softness, others a "thinness", "smoothness", "fullness", "body", "gloviness", and so on. Such terms as these are more or less qualitative in their evaluation. Nevertheless, they are recognized and accepted by the finisher and the converter and represent the specifications which the finished cloth must meet. So many different types of finishes are produced that the finisher finds it necessary to have quite a varied supply of finishing materials at his disposal. A sulfonated oil does not always exhibit the same finishing properties in all mixtures or on all fabrics. For instance, an oil may be used to produce a very soft finish on a certain type of cotton cloth. Another piece of similar cloth requires more weight or "body", which may be obtained by the addition of starches or dextrines. It will often be found that the oil used to produce softness in the first case will have very little softening effect in the second case, where it has to lubricate and soften not only the cloth but also the starch or dextrine film. Again, if the same finish is required on a rayon or acetate silk fabric, different oils entirely must sometimes be used.

I would like to attempt at this point to generalize somewhat on the uses of finishing oils. On cotton, where a thin, soft hand is required, satisfactory results are usually obtained by the use of straight sulfonated low titre oils or by compounded oils. By low titre oils, I refer to any titre of less than 25° C. Any of the following oils may be found suitable for this type of finish: sulfonated olive, castor, tea seed, red or corn oils, or any of these compounded with a white mineral oil of 75 seconds* or higher. If more fullness or apparent weight is desired, an oil of somewhat higher titre is used, such as tallow or palm oil. If still more fullness is desired, emulsions of stearic acid, palmitic acid or the various waxes, such as Japan, paraffine or carnauba may be employed. On the other hand, if a stiffer finish is wanted with more body, or apparent thickness and weight, it is usually found necessary to incorporate starches, dextrines, gums, or glucose in the finishing mixture. For softening this type of mixture, the low titre oils are found to be not so effective as the high titre oils, or saponified oils and emulsified waxes. Sulfonated tallow, partially saponified tallow or stearine, and emulsified stearic or palmitic acids are excellent softeners for finishes of this nature.

In the finishing of rayon, the problem usually becomes one of softening the cloth to a maximum degree, and for this purpose the low titre sulfonated oils and compounded oils, which penetrate readily between the individual filaments, find the widest appilcation. Before the advent of low luster rayon fabrics, the higher titre oils and waxes were of no practical value in rayon finishing, due to the fact that they tended to obscure the high luster of the rayon fiber. In the past year or two, however, the demand has been more and more for rayon fabrics with subdued luster. These delustered effects are obtained by the incorporation of titanium oxide in the rayon spinning solution, or by the application of this pigment, or other white pigments, to the cloth in the finishing bath. With these delustered effects in vogue, it has been found possible and

*Oils consisting of a solvent and an emulsifier such as sulfonated oil, soap or naphthene sulfonates.

*Saybolt viscosity at 100° F.

advantageous to employ the higher titre sulfonated oils, and also waxes, for obtaining certain finishes on rayon fabrics.

In the finishing of acetate silk fabrics, very little oil or other finishing materials are used due to two factors. First, the acetate yarn is composed of filaments which are practically impervious to water and, consequently, aqueous dispersions of oils have little effect since they cannot penetrate the yarn; and secondly, almost any desired finish may be obtained on an acetate fabric by the proper mechanical manipulation in the plant. The only oils used to any extent in acetate silk finishing are highly sulfonated olive and castor oils, sometimes combined with solvents to aid penetration.

The following list of oils, waxes and their derivatives will give an idea of what is being used for the finishing of cotton and rayon cloth (listed approximately in the order of the quantities consumed): Tallow, Castor Oil, Olive Oil, Stearic Acid, Mineral Oil, Red Oil, Japan Wax, Cocoanut Oil, Paraffin Wax, Palm Oil, Tea Seed Oil, Stearine, Peanut Oil, Cottonseed Oil, Corn Oil, Fatty Alcohols, Bees Wax, Palmitic Acid and Carnauba Wax.

I would like to mention some of the specifications which a finishing oil should meet. The finishing of cotton and rayon fabrics differs from the finishing of pure silk particularly in this respect. In silk finishing large amounts of soluble heavy metal salts are used for adding weight to the fabric. The salts would quickly precipitate most of the ordinary sulfonated or emulsified oils on the market. For this reason, it is necessary to use highly sulfonated oils which are resistant to the action of these compounds. On the other hand, in cotton and rayon finishing, it is seldom that heavy metal salts are used in the finishing bath and, consequently, less highly sulfonated oils are usually satisfactory.

The most apparent qualities of a finishing oil which have an important bearing on its suitability, are color and odor. As these oils remain in the fabric until it reaches the consumer, it is of prime importance that they possess no disagreeable odor or objectionable color.

The next specification is that the oil shall form a stable emulsion in water. This property may be fairly well demonstrated in the laboratory by two simple tests. First, 10 cc. of the oil is poured into 200 cc. of boiling water. The mixture is allowed to boil vigorously for 5 minutes and then allowed to stand quietly for 2 hours. The second test consists of pouring 10 cc. of the oil into 200 cc. of cold water (15° C.) and heating it to a boil. It is then boiled vigorously for five minutes, and finally allowed to stand quietly. If, at the end of two hours, either of these two solutions shows any sign of oil globules or scum on the surface, the oil should be considered unsafe for use. Any separation of this type in the plant is liable to get onto the cloth, causing oil-spots and blotches, which are sometimes quite difficult to remove.

Some finishing oils tend to oxidize quite rapidly after being applied to the cloth. This oxidation usually results in the development of objectionable odors and discolorations. This tendency should be carefully guarded against in a finishing oil, as it is the basis of a good many claims for which the finishing plant must settle. These oxidation effects are sometimes not apparent until after the finished cloth has been packed in cases and stored away for several months. In the laboratory, it is possible to determine in advance whether an oil is apt to develop these objectionable properties. A piece of clean, white cloth is passed through a solution of the oil containing the equivalent of 7.5% of actual fatty matter. The strip is then passed through squeeze rolls to remove excess solution. It is then folded and rolled up so that it will fit into a 4 oz. screw cap jar. The cloth is placed in the jar, the cap screwed on tight, and the jar set in a constant temperature oven at 50° C. for a period of two weeks. During this period, the cap is removed from the jar for a minute or two once every day to insure an ample supply of oxygen at all times. If, at the end of this period, the cloth has developed a decidedly rancid odor or has yellowed at all, it should be considered unfit for use. Ordinarily, one would assume that a sulfonated oil made from an oil of low iodine number would be less likely to oxidize than one made from an oil with a high iodine number. This does not hold true, however, because a poor sulfonation of a low iodine oil may cause a "cracking" of some of the larger fat molecules with the subsequent formation of lower molecular weight, unsaturated compounds. Then again, with proper sulfonation and aftertreatment, a relatively high iodine oil may yield a product which is quite free from any tendency to oxidize.

There are several other specifications of minor importance which finishing oils are sometimes called upon to meet. However, time will not permit me to discuss them in this paper.

Most of the requirements and specifications which are imposed upon the sulfonated oils of today by the textile industry are dependent not so much upon the characteristics of the raw oils from which these products are made, as upon the properties which the sulfonated oil manufacturer has been able to incorporate into his product. In other words, the choice of raw materials for use in the manufacture of finishing oils is not so important as are the methods by which they are sulfonated and aftertreated. Sulfonation may alter the chemical and physical characteristics of an oil to such an extent that, as far as analysis is concerned, the oil is unrecognizable. The iodine number, titre, saponification value, acetyl value and the color and odor may be greatly changed. The finished oil may contain large or small amounts of organically combined sulfur trioxide, free fatty acids or combined alkali. Each and all of these active groups are dependent, not so much upon the raw oil as upon the method of manufacture; and upon these characteristics of the finished product depend its usefulness in the processing of textiles.

Principles of

Dyeing with Acid Dyes*

By L. R. PARKS and P. G. BARTLETT

Dyeing with acid dyes is an adsorption phenomenon analogous in every respect to the adsorption of inorganic acids by charcoal. Acid dyes are organic color acids which contain the color in the acid radical, dissociate in water to give colored anions, form true aqueous solutions, and are taken up by the fiber as the color acid. The amount of acid dye adsorbed is dependent on the hydrogen ion concentration of the dye bath. Sodium sulfate decreases the hydrogen ion concentration of acid dye baths.

THE various theories proposed to account for the mechanism of dyeing are commonly classified either as chemical or physical. In the former class are grouped those explanations which assume that a chemical reaction takes place between the dye and the fiber or between constituents of each. The latter class assumes that the process consists fundamentally of an adsorption of the dye by the fiber. In the consideration of the application of the dyestuff to the fiber the coloring matters must be classified according to the modern theories of solutions and colloids.

Such a classification has been proposed by Parks and Beard[5] who define acid dyes as organic color acids, which contain the color in the acid radical, dissociate in water to give colored anions, form true aqueous solutions, and are removed by the fiber as the color acid. According to this definition dyeing with acid dyes should be analogous to the adsorption of inorganic acids by charcoal.

It is well known that hydrogen ions are the most strongly adsorbed, and that the adsorption of hydrochloric acid or nitric acid may be increased by the addition of a salt with a common ion, while on the other hand the adsorption may be decreased by the addition of sodium sulfate. Therefore sodium chloride is an assistant for the adsorption of hydrochloric acid, and sodium sulfate is a restrainer. Furthermore, sodium sulfate is a restrainer for the adsorption of sulfuric acid.

It is the purpose of this paper to show that the behavior of acid dyes towards adsorbents is similar to the behavior of hydrochloric acid and nitric acid towards charcoal.

EXPERIMENTAL PROCEDURE AND RESULTS

A. The Effect of Inorganic Salts on the Adsorption of Inorganic Acids

The charcoal used in these experiments was prepared by charring sugar in platinum dishes and finally heating in covered porcelain crucibles in an electric furnace, which was kept at about 1000° C., for 48 hours. This charcoal was then ground in an agate mortar, to pass through a 200 mesh sieve, and thoroughly mixed. prepared in this manner is an active Charcoal prepared in this manner is an active adsorbent and contains less than 0.2% ash. All solutions were prepared with conductivity water. The acids were Baker's "Analyzed" and the salts were Merck's "Reagent" products. All of the experiments were performed with 0.0100 N acid prepared as follows: 50 cc. of the 0.1000 N solution was mixed with a definite amount of salt solution in a 500 cc. graduated flask, and diluted to volume. This method gave solutions of the desired neutral salt concentration, which were 0.0100 N with respect to the acid present. For example, with hydrochloric acid, the acid in each sample was 0.01 N, but the concentration of the sodium chloride was increased in successive samples from 0 to 4.5 N; 4.5 N is the normality nearest to the saturation point with which it is practical to work. Before treating the charcoal these solutions were titrated with 0.01 N standard alkali as an assurance that the prepared solutions were exactly 0.0100 N. Phenol red (phenolsulfonephthalein) was used as indicator.

From each solution two 125 cc. portions were taken. Each portion was shaken with 1.2500 g. of charcoal in a 500 cc. Erlenmeyer flask. The flasks were placed in a constant temperature bath and kept at 25° C. for 24 hours. This gave ample time for equilibrium to be reached. The charcoal was then removed by filtering. Fifty cc. portions were titrated again, using 0.01 N standard sodium hydroxide. The difference in the concentration before and after treatment with charcoal indicated the amount adsorbed. According to this method two 50 cc. portions were titrated from each sample and two samples were taken for each salt concentration. This gave four measurements for each result reported.

The results are tabulated in Table I and shown graphically in Fig. I. The values (x/m) are stated in milligram equivalents of acid adsorbed per gram of charcoal.

*Contribution from the Pond Chemical Laboratories of the Pennsylvania State College.

TABLE I

Adsorption of 0.01 N Mineral Acids in the Presence of Increasing Concentrations of Their Sodium Salts

Hydrochloric Acid		*Nitric Acid*		*Sulfuric Acid*	
NaCl.N	x/m	$NaNO_3$.N	x/m	Na_2SO_4.N	x/m
0.00	0.0537	0.00	0.1465	0.00	0.0793
.10	.0562	.10	.1845	.10	.0559
.20	.0685	.20	.2039	.20	.0335
.30	.0780	.30	.2093	.30	.0246
.50	.0912	.50	.2206	.50	.0195
.75	.1079	.75	.2322	.75	.0149
1.00	.1150	1.00	.2462	1.00	.0079
1.50	.1245	1.50	.2574		
2.00	.1395				
2.50	.1450	2.50	.2942		
3.50	.1711	3.50	.3124		
4.50	.1917	4.50	.3321		

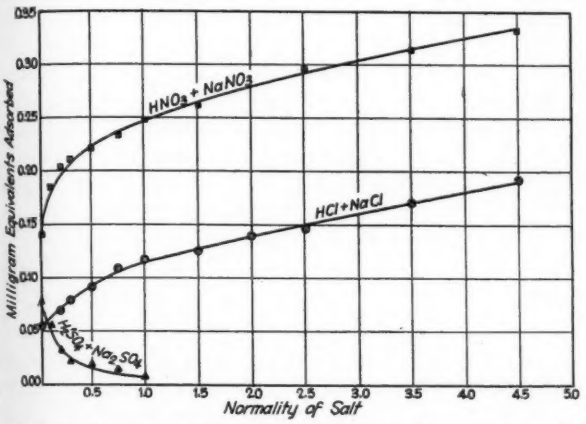


Fig. 1—The Adsorption of 0.01 N Mineral Acids in the Presence of Increasing Concentrations of Their Sodium Salts.

The amount of hydrochloric acid adsorbed increases rapidly with increased concentration of sodium chloride up to about 0.75 N concentration of salt. With more concentrated solutions, in respect to the salt, the increase in adsorption of the acid approaches a linear function of the increase in salt concentration. The presence of sodium nitrate affects the adsorption of nitric acid in the same manner. Nitric acid is adsorbed to a greater extent than hydrochloric acid. The amount of sulfuric acid adsorbed decreases as the concentration of sodium sulfate increases.

In order to show that sodium sulfate acts as a restrainer in the adsorption of hydrochloric acid and nitric acid, a solution of each acid was prepared which was 0.01 N with respect to the acid and 1 N with respect to sodium sulfate. The results are given in Table II.

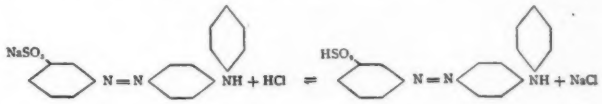
TABLE II

Adsorption of 0.01 N Hydrochloric Acid and 0.01 N Nitric Acid in the Presence of Sodium Sulfate

Hydrochloric Acid		*Nitric Acid*	
Na_2SO_4.N	x/m	Na_2SO_4.N	x/m
0.00	0.0537	0.00	0.1465
1.00	.0381	1.00	.1010

B. The Effect of Inorganic Salts on the Adsorption of Acid Dyes

The methods used in this work were for the most part similar to those used by Briggs and Bull[1]. The adsorbents consisted of activated sugar charcoal and unbleached thoroughly washed wool. The wool had an ash content of 0.26 per cent. All salts were of "Reagent" grade. The Acid Form of Metanil Yellow was prepared from Metanil Yellow by the addition of hydrochloric acid. This reaction may be represented by



To determine the effect of electrolytes in the dyebath, the amount of dye was kept constant in each solution and the amount of electrolytes added was varied. 250 cc. of each solution were mixed with an accurately weighed sample of adsorbent which weighed approximately two grams. Each 250 cc. of solution contained 87.5 milligrams of Metanil Yellow, 4 cc. of 0.1 N HCl, and a certain number of cc.'s of tenth normal electrolyte which varied with each sample. The solution and wool mixtures were boiled under reflux condensers for forty-five minutes, the wool was then removed immediately from the solution, the remaining solution cooled, and aliquot portions titrated with titanium chloride solution. Experiments in which charcoal was the adsorbent were carried out in a similar manner. Exactly two grams of charcoal were mixed with 250 cc. of solution and held just under the boiling point for forty-five minutes, and filtered while hot. Approximately the first thirty cc.'s of filtrate were discarded to allow for the removal of some of the dye by the filter paper. Titrations were performed as before.

Aliquot portions of the original solutions, not mixed with the adsorbent, were also titrated. Thus it is possible to determine the original concentration of the dyebath, the concentration of the dye in the bath after dyeing, and by difference, the amount of dye removed by the adsorbent.

The effect of varying concentrations of electrolytes in the removal of the dye from solutions of constant dye concentration are shown in the subsequent tables. Whether charcoal or wool is used, the results are in every case analogous. Increasing amounts of dye are adsorbed, as the concentration of hydrochloric acid added, increases. Sodium sulfate, secondary sodium phosphate, and sodium tetraborate, all lessen the amount of the Acid Form of Metanil Yellow removed by charcoal or wool.

TABLE III

Adsorption of the Acid Form of Metanil Yellow in the Presence of HCl

	Charcoal as Adsorbent			*Wool as Adsorbent*		
cc. 0.1 N HCl	Grs. of Charcoal	Mgs. Dye Adsorbed	x/m	Grs. of Wool	Mgs. Dye Adsorbed	x/m
0.0	2.0000	22.14	11.07	2.0281	32.89	16.22
1.0	2.0000	25.64	12.82	2.0247	51.49	25.44
3.0	2.0000	32.04	16.02	2.0021	67.02	33.48
5.0	2.0000	38.00	19.00	2.0020	71.01	35.47
10.0	2.0000	53.24	26.62	2.0191	72.39	36.00
15.0	2.0000	67.60	33.80	2.0014	73.24	36.60

TABLE IV

Adsorption of the Acid Form of Metanil Yellow in the Presence of Na_2SO_4

	Charcoal as Adsorbent			*Wool as Adsorbent*		
cc. 0.1 N Na_2SO_4	Grs. of Charcoal	Mgs. Dye Adsorbed	x/m	Grs. of Wool	Mgs. Dye Adsorbed	x/m
0.0	2.0000	53.18	26.59	2.0054	71.92	35.81
2.0	2.0000	40.66	20.33	2.0152	59.94	29.97
5.0	2.0000	35.32	17.66	2.0056	56.77	28.38
8.0	2.0000	32.35	16.17	2.0000	55.64	27.32
15.0	2.0000	31.78	15.89	2.0104	55.50	26.43

TABLE V

Adsorption of the Acid Form of Metanil Yellow in the Presence of Na_2HPO_4

	Charcoal as Adsorbent			*Wool as Adsorbent*		
cc. 0.1 N Na_2HPO_4	Grs. of Charcoal	Mgs. Dye Adsorbed	x/m	Grs. of Wool	Mgs. Dye Adsorbed	x/m
0.0	2.0000	53.18	26.59	2.0057	71.92	35.81
2.0	2.0000	36.04	18.02	2.0204	69.12	34.22
5.0	2.0000	31.68	15.84	2.0000	52.60	26.30
8.0	2.0000	28.86	14.43	2.0272	38.63	19.06
15.0	2.0000	28.90	14.45	2.0073	12.86	6.41

TABLE VI

Adsorption of the Acid Form of Metanil Yellow in the Presence of $Na_2B_4O_7$

	Charcoal as Adsorbent			*Wool as Adsorbent*		
cc. 0.1 N $Na_2B_4O_7$	Grs. of Charcoal	Mgs. Dye Adsorbed	x/m	Grs. of Wool	Mgs. Dye Adsorbed	x/m
0.0	2.0000	53.18	26.59	2.0286	72.64	35.81
2.0	2.0000	53.09	16.54	2.0241	45.56	22.53
5.0	2.0000	18.12	9 06	2.0308	15.39	7.58
8.0	2.0000	6.11	3.05	2.0268	5.39	2.66
15.0	2.0000	3.66	1.83	2.0146	4.11	2.04

DISCUSSION AND INTERPRETATION OF RESULTS

Inorganic Acids

The adsorption of an ion gives a charge to the colloidal particle which attracts to it, although less strongly, the oppositely charged ion of the electrolyte. The resultant effect is a reversible equilibrium of electrostatic forces. There is the attraction of the colloidal particle for the ion which is adsorbed. Also there is the tendency for the oppositely charged ion to diffuse through the solution, attracting to it the adsorbed ion. The direction of this last attraction is away from the colloidal particle.

The effect of the attraction away from the colloidal particle will depend upon the degree to which the ion is adsorbed. Langmuir's[3] explanation for the adsorption of gases by charcoal undoubtedly applies here. "Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom."

There is a stage in adsorption which is approximately irreversible. This has been pointed out by Parks and Keller[4] in their description of the difficulty with which part of the adsorbed acid is removed from cotton by washing with pure water. This stage, in the case of charcoal, may be pictured as the part of the hydrogen ions which are surrounded on nearly all sides by carbon atoms. Of course, if these hydrogen ions cannot be removed by washing, the anions must also remain in the charcoal or in close proximity to it. In the case of hydrochloric acid, for example, when the increased adsorption in the presence of sodium chloride occurs, the same picture is applicable. The excess of chloride ions in the solution decrease the tendency of the chloride ions of the hydrochloric acid to diffuse. Consequently, its attraction upon the hydrogen ion away from the particle is lessened. This allows the hydrogen ions adsorbed to become more firmly attached to the carbon, by penetrating further into the spaces between the carbon atoms. This penetration leaves room for more hydrogen ions to be adsorbed, although less firmly, at places nearer the surface of the carbon particle.

Since the tendency of the chloride ions, of the adsorbed hydrochloric acid, to diffuse cannot be entirely suppressed by a saturated solution of sodium chloride, a continual increase in the adsorption of hydrochloric acid with increased concentration of sodium chloride is to be expected. Up to and including 4.5 N solutions with respect to sodium chloride, no evidence of a maximum adsorption of hydrochloric acid was discovered.

The adsorption of nitric acid from sodium nitrate solutions is exactly analogous to the case already considered. The fact that nitric acid is more strongly adsorbed than hydrochloric acid shows that although both the nitrate and chloride ions are less strongly attracted to the charcoal than are the hydrogen ions, the nitrate ion is more strongly attracted than the chloride ion.

It is well known that more acid is adsorbed per gram of adsorbent if the hydrogen-ion concentration of the solution is increased, and that less acid is adsorbed if the hydrogen-ion concentration of the solution is decreased The quantitative adsorption of dissolved acids in relation to the end concentration can be expressed by the equation

$$x = a.\ C^{1/n}$$

where x is the amount adsorbed by one gram of the adsorbing material, C is the equilibrium concentration of the solution after adsorption, a and n are constants depending on the nature of the acid and the adsorbent. The value of the exponent (1/n) is less than one.

The decrease in the adsorption of sulfuric acid in the presence of sodium sulfate is due to the decrease in the hydrogen ion concentration. Thomas and Baldwin[6] have shown that sodium sulfate decreases the hydrogen ion concentration of acid solutions. The reaction

$$H_2SO_4 + Na_2SO_4 = 2NaHSO_4$$

undoubtedly takes place to some extent. The greater the concentration of the sodium sulfate the more sodium acid sulfate will be formed. With an excess of sodium sulfate, the sodium acid sulfate will liberate few frec hydrogen ions. Consequently, the higher the concentration of the neutral sulfate, the fewer the hydrogen ions in the solution available for adsorption.

(Continued on page 495)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

AUGUST 26, 1935

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Headquarters — Read House

STANDARD SILK SAMPLES

There have been prepared, under the direction of the Sub-Committee on Fastness to Dyed Silk, standard dyed silk fabrics to represent four classes of fastness to washing—namely, Class I, Class II, Class III and Class IV. These standards have been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1931 Year Book.

The A.A.T.C.C. is prepared to furnish sets of these washing standards for a nominal charge which will cover the cost of preparation. It will be possible to accurately grade the fastness by comparing it with the standards after subjection to the standard washing tests approved by this Association. All inquiries concerning these Silk Washing Standards may be addressed to the Chairman of the Research Committee—Louis A. Olney, Lowell Textile Institute, Lowell, Massachusetts.

Proceedings of the American Association of Textile Chemists and Colorists

White Oils*

By KARL T. STEIK†

I SUPPOSE, rather recently, the so-called white oils have come into use in the textile industry, and when the chairman of your Program Committee asked that someone from our laboratory be the speaker of the evening, the notice was rather short, and we all were somewhat handicapped. Someone suggested that it might be of interest to you to have something said about the white oils. So, since I had been in the petroleum industry, I was delegated to do that.

Petroleum as it comes from the ground, perhaps with one exception, is usually a very dark liquid, and as such probably the only use it has is just as a source of calories. Before petroleum can be applied to any industrial uses, it has to be modified in some way or other.

The composition of petroleum is rather complicated, and there are no abrupt steps or no abrupt types of petroleum which differ to any marked extent from each other. If I should make a comparison, petroleum is like the climate. As you go from North to South, you have a gradual transition, and the uniformity of the climate will depend on how wide an area you consider. The area in this case would correspond to so-called cuts of the petroleum that you get during the distillation. Not only do you have to consider that in the case of climate, but you also have to consider the altitude changes.

Since petroleum products generally sell at comparatively low prices, the processes of refining cannot be very elaborate, at least not very costly, and mechanical processes are used to a great extent.

The very first thing that is done in refining petroleum is fractional distillation by means of distillation. Then a great deal of the non-volatile impurities are left behind in the so-called still residues.

The distillates obtained are still full of all kinds of impurities. When I say impurities, I mean compounds or molecules other than those containing just carbon and hydrogen, molecules that contain oxygen and sulfur predominantly, and to some extent, also, nitrogen.

These impurities, oxygen and sulfur containing compounds are undesirable for a good many reasons. Sulfur compounds as a rule contribute to the dark color, they might contribute to the corrosion, and also to the odor of the distillates, and therefore they have to be removed. Oxygen compounds are predominantly acids, and the acids that are best known, which have their origin in petroleum, are the so-called naphthenic acids.

The refining of petroleum, the chemical side of the refining, is rather rudimentary. Years ago it was discovered that sulfuric acid had very marked visible effect on petroleum, that some of the impurities were coagulated and some dissolved in the acid, and as a result of such agitation with the sulfuric acid there was improvement in color and odor. That method is still largely used at the present time.

I think it is rather characteristic that chemists are curious and someone—this happened to be in Russia—noticed that the treating of petroleum distillates could be extended beyond the degree that is required for common industrial products. He kept that treating up and finally got more and more improvement of color, lighter oil, less odor and less taste. So he decided that if, say 60° Baumé acid does all that, perhaps a stronger acid would do something more, making it more desirable, so he went into 100 per cent acid and finally ended with fuming acid. As a result of that treatment, by persevering, this man, Gregory Petrov, obtained what at that time was known, and is still known to some extent, as Russian white mineral oil.

Because the treatment is so severe with fuming acid, perhaps there exists an impression that that makes the composition of the final product, of the white oils, rather uniform. I don't believe that that is the case.

We are still hanging on too much to the old groups of organic compounds that you find in the textbooks. These are the paraffins, here, and in the next section there you have the aromatics, and then the terpins and what not, as if they were separate groups. I just want to call your attention to how many strictly aromatic compounds there are. I know only one and that is benzene itself. The minute you put in some paraffinic side chain, the compound no longer is strictly aromatic. You immediately get the properties of the paraffin hydrocarbons, and the paraffins are considered inert, having little activity, and therefore the desire, I suppose, existed to get an oil that was strictly composed of paraffins in order that it would be stable against chemical changes.

* Presented at meeting, N. Y. Section, April 26, 1935.
† Director of Research, National Oil Products.

I think it is rather inadequate to call these non-nuclear molecule hydrocarbons, paraffinic.

I have been speculating why they have been called paraffins and have come to the conclusion that chemists called them paraffins not because they were not reactive, but because they reacted in such a way that the chemists did not want them to react. The possibilities were rather enormous, and the control of the reactions difficult. Therefore, they simply, as an excuse, called them paraffins, not because they didn't react, but because they didn't react in the way they would have liked to have them react. When you stop to think that with only three hydrocarbons in the molecule there are something like, well over 20, anyway, oxidation products, and a good many of them already are known, the reactivity is quite considerable. In the petroleum you have all kinds of these groups. You have the paraffin hydrocarbons, you have the aromatic hydrocarbons, and then you also have the naphthenes. The naphthenes, particularly, are very little known. Since the time that they were discovered by Markovnikoff some 25 or 30 years ago at the University of Moscow very little has been done about them, and there are wrong conceptions existing concerning them.

They are also assumed to be quite non-reactive, because the ring, whether it be a five or six membered ring, or seven or even more, is entirely saturated. The naphthenic nucleus doesn't have any double bonds like the benzene nucleus, and the natural conclusion has been that therefore they are very non-reactive compounds, and perhaps that is also why some sulfonated naphthenes or naphthenic acids are still considered naphthenic. Sulfuric acid can act as oxidizing agent with certain compounds under certain conditions. When going through a petroleum refinery, very likely you will notice the smell of sulfur dioxide. This gas is a direct evidence that sulfuric acid had acted as an oxidizing agent when in contact with petroleum. The extent of the oxidizing action depends on the composition of the oil, concentration of the acid, temperature, efficiency of distribution of the acid in the oil and the type of agitation. Because of the oxidizing action of sulfuric acid, fuming acid particularly, the naphthenes suffer greatly.

Picture a benzene ring with CH_2 groups at its corners and you will have the simplest naphthene with a six carbon atom ring. This ring may be oxidized in steps, thus approaching the structure of benzene. Such products of oxidation are found in the acid sludge as such or in combination with sulfuric acid. Of course, substitutions will change the behavior of the naphthenic ring.

No one petroleum fraction, unless it is the very light fraction (say pentane, hexane, heptane and octane) is composed of hydrocarbons of one group only. They all contain the paraffin hydrocarbons, I mean open chains, and the aromatic and the naphthenic. The reactivity of the open chain hydrocarbons depends on the structure rather enormously. I don't know whether any of you have had occasion to try it, but whenever you run across a tertiary carbon atom in the molecule, you find that it is extremely reactive. It will reduce permanganate, for example, in the cold. To call paraffins non-reactive is quite far-fetched.

The purpose of refining an oil to such an extent as to finally end up with a white oil, naturally was to treat the oil long enough to remove all the rather reactive compounds and end up with an oil fairly stable or fairly non-reactive chemically.

That stage is never reached by acid treating alone, whether it be just ordinary sulfuric acid or fuming acid that contains free SO_3. By treating with acid alone it is difficult to make white oils. The acid always reacts, and because of the reaction, there are always colored substances produced. In order to eliminate colored substances formed in the treating, physical means have to be used. Various absorbent clays, like Floridin clay, that absorb the colored molecules, are used. That is how, finally, the oil is made white.

White oil prepared in that way still would not be suitable, let's say, for medicinal purposes. It would not consist of hydrocarbons only, because in the reaction with sulfuric acid there are two main by-products formed. One is the so-called acid sludge which is not very troublesome because it usually precipitates out. There is another type of sulfonated compound formed which remains in solution in the oil, and this has to be removed. That removal is done by means of some organic solvent, such as aqueous alcohol or acetone. The solvent has to be such that it must naturally not be miscible with the oil, otherwise you will not get layer separation. You ordinarily use some organic solvent which as such may be miscible with the oil, but when water is added to it, then it is no longer miscible in oil and precipitates out, and the layers are formed.

That is where Petrov's discovery really came in: to find out how to remove these oil soluble sulfonic acids. If I mention contact perhaps or mahogany acids, or mahogany soaps, then you may know what I am referring to. These acids are used in splitting fats, they are very effective, and because they are stable, the sulfonic group doesn't split off, and the sulfonic group in the acids doesn't act as an oxidizing agent under the conditions of fat splitting. Therefore the fatty acids and glycerin obtained by that procedure are of much lighter color and are more desirable.

Originally, these white oils were used only for medicinal purposes, and for that reason the viscosity of the oils had to be such that their flow through the digestive system could be somewhat controlled. Naturally, in order to be sure that these white oils would have no undesirable physiological effects, it was assumed that if these oils didn't react to any appreciable extent with concentrated

sulfuric acid then they should go through the system very much unchanged, and that is how the so-called sulfuric acid test came in. You take equal volumes of concentrated sulfuric acid and the oil, heat it for 10 minutes at 100° C., shake it every two minutes, and then afterwards determine the color of the sulfuric acid. The lighter the color of the sulfuric acid after contact with this oil for ten minutes the better it is.

That is perfectly all right for medicinal use. However, for technical application, that may not be quite so desirable.

Unfortunately, the trade or the consumers expect that the products they buy should have some talking point—it is the same on the selling side of it—that can be emphasized, and if the talking point has all kinds of appeals—sight, odor and taste—that is much better. So the manufacturers of white oils have—some of them anyway—gone to extremes in emphasizing these points: 30 plus color on a scale where 18 is already so-called water white. If the oil is nice and brilliant, well, it must be good. If it has no odor and no taste, it must be still better.

I say the consumer doesn't known that such a high degree of refining might be detrimental. I imagine every one of you has heard about the anti-oxidants that are used in oils to keep them from oxidizing quite as rapidly as they might naturally oxidize. That refers to animal and vegetable oils, and also refers to mineral oils.

It seems to me, at least, that the anti-oxidants that are naturally present in oils are just as effective as the artificial ones that we put in subsequently, and may be more effective. In this extreme refining, the natural anti-oxidants are apt to be lost entirely. Since in white mineral oils no anti-oxidants are put in, such oils might oxidize quite rapidly. That oxidation takes place, I imagine all of you know, when you take a piece of white paraffin wax, a solid wax, or if you take a jar of highly refined so-called water white petrolatum (vaseline), and put it out in the sunshine, it may not take more than a half hour or an hour for you to be able to notice a yellowish tinge. Oxidation took place.

Therefore, in this so-called high acid test, when you shake up the oil with the sulfuric acid, and your acid is not at all or very little discolored, take that with a grain of salt. It may not be just what you want, although it may be a good thing for some purposes.

The oils, petroleum oils, or such white oils as are used in the textile industry are limited rather to the low viscosity oils. I suppose in textile oils you want only very little lubrication. You don't talk about three, four, five or ten thousand pounds of pressure per square inch, but only a little. If you go into high viscosities you have more friction. Instead of getting lubrication, you are getting the opposite effect. So the use is limited to the lower viscosity oils. Lately, oils are being used that are almost as low in viscosity as kerosene. There you would have low viscosity, but you would run into another trouble. The oil would not stay on your yarn or on your fabric long enough. It would evaporate too rapidly.

I imagine in most instances the oil that is applied to the textiles, before dyeing, anyway, has to be removed, and therefore these white oils, like vegetable oils, have to be made emulsifiable. Petroleum oil has really unlimited possibilities. It is rather unfortunate that the petroleum industry hasn't taken advantage of the by-products that are formed in manufacturing the white oils.

I mentioned that you have there, as an impurity, the naphthenic acids. Naphthenic acids, the soaps, are really soluble in oil, not only the sodium and potassium soaps, but also the soaps of heavy metals like lead, aluminum, and calcium. Unfortunately, these naphthenic acids have rather an undesirable odor, which is not characteristic of the acids themselves but of the impurities that go along with these acids while they are being extracted from the oils. If the odor of naphthenic acids could be removed by some process that is not too costly then there would be a base for a good emulsifier, originating from the petroleum oil itself.

However, the other by-product that I mentioned, the so-called mahogany acids or mahogany soaps, or the contact are gradually coming into more use as emulsifiers in the textile industry.

They have an advantage over ordinary emulsifiers because they are true sulfonates. That is, the SO_3H group is directly bound to the carbon atom, the sulfur to carbon bond, and since the composition of the rest of the molecule is saturated, they are not changed much by ordinary oxidation at room temperature or even at higher temperatures.

This statement applies to mahogany soaps that have been purified so as to remove the soap of sludge acids. If this has not been done, then there will be much darkening of the color on heating because the sludge soaps are quite readily decomposed by heat. Because of this decomposition free sulfuric acid may be formed, and it may have a detrimental effect on the fibers. In an attempt to remedy this difficulty, the mahogany soaps, as a rule, contain an excess of alkali.

At the present time fairly pure mahogany soaps are available. And yet, fairly large quantities of them (up to 30%) have to be incorporated in oils in order to make them readily emulsifiable. Because of the high concentration of the soaps in the oil the viscosity of the latter becomes too high for free running of the yarn during the mechanical operation. The result is, that mahogany soaps as yet are not ideal emulsifiers.

The other by-product, the sludge, is also very interesting, but because of its color it has no particular value. Chemically, it is very interesting, but I imagine it in time will go into oblivion and the chemist will never know what its composition was. This acid sludge is a nuisance,

and instead of trying to make something useful out of it, it was cut back with some cheap fuel oil and burned under the stills. The still man used to kick because of the fumes and the bottoms of the stills corroded, so other means of destroying it had to be devised. Now, the acid sludge is being heated to break down the sulfur compounds to form sulfur dioxide. The sulfur dioxide with the catalyst, platinized asbestos, or vanadium by the contact sulfuric acid process, is oxidized to SO_3 to make sulfuric acid. The time may come that the sulfuric acid in the petroleum refinery will be regenerated with some replacement for loss in the process.

The part, perhaps, in which you will be more interested in connection with white oils is the oxidation. As I mentioned before, white oils were started in the textile industry primarily for color, because being colorless, they didn't add any color to your textiles and also because they are relatively stable on oxidation. However, they are not immune. They do oxidize.

In regard to oxidation, I think the main difference, apart from the rate of oxidation, which is much slower in the case of white oils, is that when white oils oxidize, the products of oxidation, as a rule, will be colorless, and do not have as undesirable an odor as a petroleum oil that has not been refined to such a degree. You can take a medicinal white oil and oxidize it by blowing air at high temperatures, say temperatures much higher than you would ever have in the textile industry, and the product will still be colorless or nearly so. On prolonged oxidation the residual oil may have the consistency of jelly; that refers to oxidation in glass. But in presence of traces of copper, then the oxidized oil will be dark, even black. So, white oils are not entirely as immune as they are sometimes expected to be.

The white oils do not differ from other oils, also, in regard to the oxidation which is autocatalytic. At first, the oxidation is very slow, and then apparently some of the products accelerate the rate of oxidation, so that if you will plot your cc.'s of oxygen absorbed against time, you get a rather flat slowly rising curve then it will go up very rapidly and apparently there is no limit to oxidation. You can get oxygen to the extent of 20 or 30 per cent of the oil.

Various products are formed: unsaturated hydrocarbons, alcohols, aldehydes, ketones, acids, esters and products of polymerization. Besides, oxidation goes much further. You have actual splitting off of individual carbon atoms in oxidation of white oils, as indicated by the presence of carbon dioxide and water. So a part of the molecule, at least, has been completely oxidized.

Except for the catalytic effect, when you get these rather dark products of oxidation, the white oil products of oxidation are much more readily removed afterwards. They do not form such resinous oxidation products, for which it is hard to find a suitable emulsifier or a solvent. That is an advantage, I imagine, in the textile industry, because even if the oil on the fibers has been oxidized, still it can be removed quite readily.

Then white oils may also have another advantage that perhaps has not been especially mentioned, and that is in connection with their effect on the skin. Those of you who had the opportunity to hear Dr. Fizer's paper on some of the compounds that produce cancerous growths will be interested to know that some compounds like that exist, at least in some petroleum oils, although white oils apparently have these compounds entirely removed. So white oils are quite safe, I should say, normally as far as their effect on the skin is concerned.

That, however, doesn't apply to oils of very low viscosity. I wouldn't say that—not referring to cancerous growths but to the drying effect—kerosene that has been treated so it is water white, or extra white 30 plus color and practically has no odor, would be entirely harmless to the skin. The chances are there would be no reaction. But because of the diffusion of the fat from the skin into the oil, there will be loss of oil and the skin may become quite brittle. But that is not really a pathological case.

I have given you sort of a short sketch of what the white oils are, how they have been made, and their general characteristics. It might be of interest, also, to mention that sometimes when you are using white oil and have taken all kinds of precautions, say, even against oxidation, have kept the white oil in a sealed bottle under an inert gas like nitrogen or carbon dioxide, and when the sample was fresh it was perfectly all right, was odorless and tasteless, and after a while that oil developed a rancid odor, and you wonder, what could have happened? The atmosphere was neutral, it was kept in the dark, and yet the oil has gone—let's use the common expression—sour. Such instances are not very many, but white oil, although it is composed strictly of hydrocarbons only, is not immune to bacterial action.

Some 25 or 30 years ago, Tauzch first discovered that there are bacteria that can make use of hydrocarbons. So when you get to a point like that, when you don't know what might have been the cause, it is worthwhile to investigate. Maybe some bacterial action took place.

I think I will stop at this point and leave the rest of the time for some questions that you may have. (Applause.)

DISCUSSION

Chairman Freedman: Thank you, Dr. Steik.

We have just listened to a very interesting, and in my opinion, highly learned discussion on white oils and on petroleum oils in general, and to me, for one, who has been handling mineral oils of various types, ranging from fuel oils all the way down, or up, I might say, to high grade medicinal oils, this subject has been most enlightening.

From the textile angle, I am quite sure that there ought to be quite a number of questions.

Mr. Schmidt: I was thinking, Dr. Steik, that the men might be interested in figures as to how much oil is destroyed by making a white oil and the approximate quantities of acids that are required to produce a white oil.

Dr. Steik: As to the amount of oil destroyed in the process of making white oils, that is relative. That depends on the initial oil. If you start out with Pennsylvania oil, your loss probably may not exceed 25 per cent. If you take Coastal oil, for example, your loss might be as high as 50 or 55 per cent before you reach the white oil stage. You have to take into consideration all of the impurities. In the case of Coastal oil, you have to take all that asphaltic material out. Most of the naphthenes are oxidized. Of course, all the original unsaturated compounds that were in the oil must be removed because you end up with a white oil that certainly should not have an iodine value higher than possibly .2. Usually it is less.

Of course, then, with the source of the distillate for making the white oil, the quantity of sulfuric acid will also vary. The more saturated the oil is, or the less compounds it contains that will react with fuming acid, the smaller your treating loss will be and the smaller the quantity of sulfuric acid used.

In the case of Columbia oil, to make a white oil, in the range of 80 or 85 viscosity (that would still be a viscosity that is used in the textile industry—I don't think you go much higher than 120 viscosity white oils) there the treating loss is about 40 per cent, and approximately 100 per cent, that is, equal weight of acid, fuming acid, is used on the original weight of the oil. Of course, that acid is not used all at once. The refining is done in steps. Start out with a given weight of crude distillate and acid is added usually in increments of 5 per cent on the oil present. This may be repeated 7 or 8 times, or maybe even 10 times, allowing the sludge to settle between successive additions of acid.

So the treating losses might be quite high, and the quantity of the acid used and the treating losses justify the higher prices that have to be paid for white oil. When considering that ordinary lubricating oil might be treated with 10-15 pounds of acid per barrel, or less, then the price of white oil, considering the expense, is quite justifiable.

Mr. Zisman: Dr. Steik, if you have oxidized mineral oil present on raw silk, would you say that soap would thoroughly remove or emulsify it?

Dr. Steik: I think it should. I would like to make a reservation there. Because the silk may come in contact, while it still has the oil on it, with various metals that might change the course of oxidation, but I don't think there should be much difficulty in removing it, particularly if, along with the soap, you use some emulsifiable oil. Soap alone as an emulsifier for these products of oxidation, from petroleum, from white oil, may not be quite efficient, but if you use an oil along with it that would act as a softener, then I think you should have no difficulty in removing it.

Dr. Harold: Is it possible that a yarn initially oiled with a portion of mineral oil, showing a perfectly neutral reaction, would grow acid in time up to the extent of actually tendering the yarn?

Dr. Steik: Yes, indeed, organic acids are formed when white oils are oxidized. Access of oxygen, temperature, humidity and time are the factors. Some very highly refined oils may oxidize sooner than less refined oils.

The extent of refining through which an oil has been subjected may be judged to some extent by the so-called hot acid test. In this test, equal volumes of oil and concentrated sulfuric acid are mixed and kept at 100° C. for 10 minutes. The lighter the color of the acid after settling, the more intense the refining of the oil. Perhaps this is because the natural anti-oxidants of the oil have been removed by the extreme refining. The protective influence of natural or introduced anti-oxidants is effective for only a limited period of time.

Various accelerated oxidation tests are made in the laboratories. They differ from each other in regard to the changes that are determined. For example, in an accelerated test the time may be noted when the temperature of the oil begins to rise above the surrounding temperature, the maximum temperature reached and time to reach it and, finally, the time it takes to cool to the temperature of the surroundings (i.e., temperature of the liquid in the jacket of the apparatus). The time interval after which the temperature of the oil begins to rise above the constant temperature of the jacket is called the induction period. The end of the induction period marks the beginning of oxidation.

A factor is established correlating the determined inhibition period, with the behavior of the oil under conditions in practice. Thus it is possible to determine approximately for what period of time the oil is safe against oxidation. The rate of temperature rise after the inhibition period and the maximum temperature reached give an indication whether the oxidation, when started, will go on rapidly or not.

While I am mentioning these facts about oxidation of oils, I do not want to be understood as admitting that oxidized oil is the only possible cause of tendering the yarn. Other substances that are on the yarn along with the oils are not absolutely wholly against the tendering effects.

Dr. Harold: Is the variation in that reaction induced by the nature of the fiber? For example, would viscose be more sensitive, not because of its original tenderness, to oxidation than cotton? Would it stimulate the oxidation? In other words, is the bed upon which the oil

exists stimulated in its oxidation by the character of the fiber?

Dr. Steik: I can't speak with any authority on your question. If there is any difference, it might be in the case of rayon which is a synthetic fiber and may contain some impurities that have not been completely removed in the processing and which may have an effect of their own. It would be interesting to carry out a temperature-rise accelerated test on some oil in contact with rayon and silk. Such a test might answer the question.

Mr. Schmeidler: Would that same statement hold for vegetable oils?

Dr. Steik: I think so. Of course, with vegetable oils, there is an enormous difference in their stability in comparison with white mineral oils.

Mr. Schmeidler: What I meant was, they would probably be less stable on silk than on rayon?

Dr. Steik: Yes, because in silk the nitrogenous matter may have some effect; also the fibers of silk are finer and, therefore, the oil will be spread over a larger surface.

Mr. Schmidt: For instance, Dr. Steik, if the white oil does undergo oxidation, naturally the acids formed are of a high molecular weight. Do these acids have greater tendering action on the fiber than, say, ordinary fatty acids, or acids of the oleic type?

Dr. Steik: It is quite natural to assume that the acids formed on oxidation of white oil are of high molecular weight. However, that is not the true story. You have high molecular weight acids formed and you have acid formed with the lowest molecular weight known, and that is formic acid. As in the composition of the oil itself, you have all gradations there, from formic acid up. The acids formed from oxidation of white oil contain around 7, 8 or 9 carbon atoms per molecule.

It looks like the molecules more or less split into such fragments. However, there always is oxidation of the end carbon atoms and those are the ones that give formic acid. Take white oil or any kind of oil, as far as that goes, that has been oxidized and distilled, and you will find formic acid and butyric acid and all those water soluble volatile acids. Those, I think, have a much greater effect on tendering than the high molecular weight fatty acids.

Dr. Harold: Dr. Steik, is there any relation between the falling off in solubility and oxidation? I have a case in mind where fuel sea oil spilled over a floor where various rayon goods were stored. The goods were badly fumed by the smell of the fuel sea oil and the colors were somewhat damaged. The blues and violets especially were changed and altered in shade by the mere fumes that spread along the floor within a few inches of the rayon goods. In the effort to redye those goods and make them salable again, the selvages did not take the color as did the bulk of the goods. Is it to be assumed that the oxidation, being more free in the selvages, played a role in producing a more insoluble product from the absorbed fumes?

Dr. Steik: Yes.

Dr. Harold: That might be a rational explanation?

Dr. Steik: Yes, that might be in the case. You see, the minute you reach oxidation to the extent where aldehydes are formed—which polymerize into resinous products that would be more difficult to remove.

Mr. Wood: Dr. Steik, you have told us a great deal about the manufacturing and the constitution of these products. I wonder if you couldn't tell us something about the application to textiles.

Dr. Steik: Well, I should have said at the beginning that I am primarily a chemist, and the question of how these various oils, mineral and other kinds, are applied in the textile industry is a dark point with me. I must confess I don't know enough about it to talk about it. If you could ask me some particular question about the properties in some instances, I might be able to answer it, but to answer in general how they are applied in the textile industry, well, maybe someone else in the room would volunteer to answer that question. I always feel that if I can't answer a question with any degree of certainty or truthfulness, I would rather not answer it.

Mr. Schmidt: I might just say a few words on the use of some of these white oils. For example, if they are mixed with soaps made from red oil and triethanolamine, or mixed with a soluble base made from soaps and alcohol, or with sulfonated oils of various kinds with enough fatty acid or other stabilizer to make the sulfonated oil and the white oil into a homogeneous mass, they then can be used for the finishing of cotton cloth, or they can be used in the oiling of wool, or as a rayon oil, and there are any number of places where the individual plant manufacturer has his own particular use which he doesn't even tell the manufacturer of the products about. So there are, as I say, a thousand and one uses to which the white oils, mixed with these emulsifying agents, can be put.

Mr. Sargent: Can the speaker define the point where it ceases to be a kerosene and becomes a stable white oil?

Dr. Steik: As far as chemical stability is concerned, your deodorized kerosene is just as stable, if it has been refined to the same degree as a white oil.

Mr. Sargent: As a white mineral oil of the same purity?

Dr. Steik: Yes, just as stable.

The instability is not chemical, only physical. Of course, kerosene has much higher vapor tension and will evaporate. That is why I suppose you can't use much kerosene. But as far as chemical stability is concerned, it is just as stable. In fact, the smaller the molecules are, the more stable they are. It is much harder to oxidize methane than the higher hydrocarbons from the chemical point of view. Kerosene is just as stable against oxidation as the higher fractions, higher molecular weight frac-

tions. The difference is in the physical properties, and, of course, in composition, too, because the lower boiling fractions are more paraffinic, and when you go into the high ones, then you get into molecules that contain either the aromatic or naphthenic nucleus with aliphatic side chains. That is the chemical difference. But for chemical stability, kerosene is just as good as the higher fractions. It is absolutely no sin to call kerosene white oil. I mean the odorless kerosene that has gone through that fuming sulfuric acid refining procedure. It is a white oil for technical uses.

Mr. Sargent: Then color is really the determining factor there, if it is white it is a white oil?

Dr. Steik: Not necessarily, no. White oil, according to the specifications, must pass the so-called sulfuric acid test mentioned before. That is the criterion for the degree of refining white oils, not for the color. Kerosene is white, too, as far as color is concerned, but shake up any kerosene that you wish with sulfuric acid and warm it up for 10 minutes at 100°C. and see what will happen to it—not only to the acid, but to the kerosene itself, too.

In the meantime, it might be worthwhile mentioning that as far as this so-called sulfuric acid test is concerned, the color of the white oil itself does not change. If it does change, then it is a sign that it is a poor grade white oil, but as a rule the color of the oil does not change, while the acid becomes colored.

Dr. Harold: Is it within commercial probabilities that in the near future, Doctor, you will have enough naphthanates to have a practical detergent based on naphthanates alone that will be free of color and odor?

Dr. Steik: When you say naphthanates you are referring to these soaps that I mentioned?

Dr. Harold: Yes.

Dr. Steik: Well, I don't know. As far as the quantity of the naphthenic acids is concerned, there is quite a lot of it available; if the unpleasant odor that is associated with some naphthenic acids could be eliminated (it can be eliminated), but then again the question comes up that the product will perhaps be too expensive.

Dr. Harold: Roughly, what would be the expected base price of a pure colorless and odorless naphthanate?

Dr. Steik: Naphthenic acid?

Dr. Harold: Yes.

Dr. Steik: If you had said just colorless, I would say around 15 cents a pound, but when you say odorless, I would say now it will cost you $1.50 a pound.

Dr. Harold: So it is not a probable competitor to Gardinols or Avirols or anything?

Dr. Steik: No. Besides, it doesn't have that effect. When you talk about Avirols and Gardinols, they have some specific effect, produce a soft handle, or whatever you call it, and feel and stretch, and all those things. That is outside of chemistry.

Chairman Freedman: I would like to ask Dr. Steik whether the doctor test is applied to white oil.

Dr. Steik: Yes. It is worth while to apply it if you have a suspicion that the oil might not be what it should be, but it is assumed that any white oil must pass the doctor test, and it must also pass the corrosion test. That is all assumed. That is part of the requirements. The doctor test is really a test for lower molecular weight mercaptans.

Chairman Freedman: The reason I asked, Dr. Steik, about whether or not the doctor test was conducted on the oils is that there appears to be an increase in the number of complaints, where irritation or erythema is alleged to result from contact with garments, and our friends in the medical profession as a rule, without evidently going very far into the situation, diagnose the case as one of poisoning due to dye. We have had occasion to run some interesting experiments along that line, and it appears that once we remove the finishing materials, the irritation is no longer there. I am wondering what the effect of sulfonated oils and probably some of these white oils may be, or what influence, rather, they may have with regard to this particular subject. I am wondering what the presence of these mercaptans might mean.

Dr. Steik: Well, white oils have been so drastically treated—they are not absolutely free from sulfur, but that sulfur is in a very inert combination.

When you say that by removing the finishing oil the trouble ceases, would it be proper to say that the finishing oil was the cause?

Chairman Freedman: Well, I don't say that it is. I am just telling you—

Dr. Steik: The fact that bodies don't react unless they are fluids, is something that is well known. The finishing oil probably acted there to make the dye fluid, to get it in solution. It was an aid, you might say, but was not the cause of the irritation.

As far as sulfonated oils are concerned—you are coming home now. Nothing is non-toxic. Everything is toxic. It all depends on the quantity. In the case of sulfonated oils, they might produce irritation. I wouldn't want to say that they are toxic. I actually mean just to say irritation. Sulfonated oils, vegetable and animal, so-called sulfonated oils, are not true sulfonated oils. You know that. In the sulfate group, the bondage is carbon to oxygen to sulfur. It hydrolyzes off and may give you sulfuric acid. Some people are very sensitive to fatty acids. I wouldn't say that the effect is exactly toxic, but some people may get a rash on the skin from olive oil, even from a grade that has 0.1 or less per cent fatty acid. But to answer as well as I can the question with regard to sulfonated oils, about the toxicity, I would say they are non-toxic. If a considerable quantity is taken internally at one time, it might be toxic.

Chairman Freedman: I might say this, Dr. Steik: We conducted a number of patch tests on individuals and we

found that those individuals were affected. In one case one of them was also affected by the adhesive tape. In another case, ordinary soap would cause a rash on the individual. There were only some isolated cases of that type.

We have yet to run across a finishing material that will produce a rash or an erythema on a number of individuals. It is generally an isolated case that pops up now and then.

There being no other questions, I would like to say, first of all, that the speaker of the evening, Dr. Steik, has really, in spite of all that he has said and the assertion of our own good P. J. Wood, proven to us that he not only is a chemist who knows his work thoroughly, but that he is also an excellent salesman. I think he has sold himself and his charming personality to the New York Section to a degree that will long be remembered. (Applause).

I will call for a rising vote of thanks.

. . . A rising vote of thanks was extended. . . .

Dr. Steik: Thank you for the compliment.

In connection with the effect on the skin, I might say—I don't know whether other companies are doing that now, too; and I somewhat hesitate about telling you this because it might sound like a sales talk, but it is not intended as such—that we are trying to find out whether an oil is safe or not, by using animals. You will find that especially white rabbits have very tender skin. Shave off the hair and allow the oils to remain on the skin say 15 minutes, half an hour, two hours, six hours, and see what the effect will be. If you want a still more sensitive test, take the albino rabbits—they are hard to get. The skin inside of the ear is supposed to be the most sensitive tissue known, and if it doesn't produce a rash there, it is absolutely safe.

I will say, however, that as far as I know, all sulfonated oils after eighteen hours produced only an edema, but for two, three or four hours the rabbit's skin will stand it.

So none of them are absolutely safe, but safe enough. It is just impossible to make it any better than that. Otherwise you have to change the characteristics of the oil to fit the skin, so to speak, and then it doesn't fit the textiles.

Dr. Coleman: Do you refer to medicinal white oils or technical white oils?

Dr. Steik: Well, technical and medicinal white oils do not differ very greatly, mostly color and acid test. Technical oils may not be so-called 30 plus color, although as far as refining is concerned, they have been refined almost as drastically as the medicinal white oils. The difference is mostly in viscosity. You know you can't use an 80 viscosity oil and drink it. You have to have a certain viscosity, otherwise the oil gets out of control, and you know what I mean by that.

Dr. Coleman: I don't agree with you, because I drank oil with 75 and 85 viscosity with no effect whatever. And I know of other cases where medicinal oil up to a viscosity of 500 was consumed and had that effect you mentioned.

Dr. Steik: To other people, not you?

Dr. Coleman: To other people.

Dr. Steik: That is perfectly natural, because you know what the controlling muscle is. It depends on whether that muscle is strong and tight, or loose. If it is strong and tight, you may drink kerosene and get away with it. If it is loose, even a thousand viscosity oil might not be in control.

Mr. Cates: Dr. Steik, may I ask you a question? This hasn't anything to do with textiles, but I was reading the other day, as perhaps you have read, that the Medical Society does not recommend the use of white oils for colds, nasal purposes. They have caused death in many instances, particularly to infants, through some effect on the lungs. I was wondering whether that effect was toxic or whether it was due to stopping up the bronchial tubes in some manner.

Dr. Steik: I don't know of any nose oil or throat oil that is just white oil. The blame there should be placed not on the white oil but what is put in the white oil. I know the ingredients of some of these nasal sprays. I don't feel quite at liberty to say what the compounds are, and why an effect such as you mentioned might take place, it is not because of the white oil.

The white oil itself, if there is no other ingredient in it besides the hydrocarbons of the oil, has a protective influence on the mucous membranes, and it should not cause injury. If it gets in the lungs, of course you know lungs function through the surface, and if that surface is covered, it would correspond somewhat to a burn, the surface would not be active any more. It may cause difficulty because of that, because of the covering effect, but not because of the toxic effect.

Mr. Cates: You mean almost an asphyxiation?

Dr. Steik: Yes, exactly that.

I know of one concoction on the market that has been barred at least in one European country because of ingredients in the oil, not because of the oil itself.

I think that is similar to where a finishing oil is blamed for some rash, when the dye or something else might have been the cause.

Mr. Cates: Doctor, the statement was made, too, that it may have been the ingredients which may have been ephedrin or menthol, but the statement was further made that white oils of any kind should not be used because there have been numerous cases of death. I don't know, it may be an asphyxiation or it may be toxic because of the tender mucous membranes of the lungs.

Dr. Steik: From the chemical point of view, there is absolutely no reason for it, and when you consider the quantity of an oil that would get into your system when you use a spray or a few drops as they recommend to you, it is too small to have enough effect, physiological effect, reaction. It may cause some trouble when under high

pressure the spray gets into the middle ear or something like that, but there the effect is mechanical, not chemical, and in the lungs I admit there may be such a thing. But I don't quite see how it would get to the lungs.

Mr. Carter: While you were speaking about oil becoming yellowish, Dr. Steik, when exposed to air and sunlight, I recalled an experience I had with some cotton cloth. This cloth, in the spinning, was oil sprayed. It went through the process of bleaching and so on, and on exposure to air and light, it developed a decidedly yellow tinge. Cloth that had not had that treatment did not. Of course, in the process of bleaching, it had gone through oxidizing action. I examined the thing and so far as I could go by the comparisons of the cloths and by process of elimination, the only conclusion I could arrive at was that there were some traces of that oil spray still in the cotton when the goods were finally bleached.

Dr. Steik: It is quite possible.

I should have mentioned perhaps that certain wave lengths have a catalytic effect on the oxidation. The same oil, if it hadn't been exposed to light, might not have caused this yellowing effect, or not in such a short time, while in light it happened more quickly.

Mr. Carter: If those goods are exposed in a store window, where you get the sunlight coming through glass, and the atmospheric oxygen—

Dr. Steik: That can happen.

Mr. Carter: Of course the amount of oil that might have remained would have been very, very small, indeed, because the spraying, I think, only amounts to about a half per cent on the weight of the cotton.

Mr. Schmidt: Only .3 of one per cent.

Mr. Carter: Well, that is enough so long as it does it. It is noticeable.

Dr. Steik: I have to admit that it can happen.

There is nothing perfect, and because these white oils have been made from mineral oil, don't associate anything in connection with mineral oil as particularly stable. Oil, no matter what kind of oil it is, is still an organic substance, and you can't change a dachshund to a St. Bernard. It is an intrinsic property of the substance. It will oxidize. The question is only in the length of time. One oil will stand longer. The inhibition period will be longer. In another one, it will be shorter. But it ultimately will happen with all of them, and light has an accelerating effect.

Mr. Carter: Of course you understand that during the process of spinning, the ultimate fibers are constantly under friction.

Dr. Steik: Yes, and besides, you have that small quantity, 0.3 of a per cent of oil, distributed over an enormous surface, with all conditions favorable for oxidation.

Mr. Carter: And color.

Dr. Steik: Yes. That is where white oils have an advantage, white oils as they should be: that products of oxidation of white oil normally are colorless, but not when exposed to light; then even they will have color. You can oxidize white oil in the absence of light or not in direct sunlight, and it will still be colorless, but certainly those short wave lengths will turn yellow.

Mr. Schmidt: Mr. Carter evidently used it quite a few years ago, and since that time all the defects that he has spoken about have been overcome.

Mr. Carter: I would like to make the remark that this matter came under my observation within the last twelve months.

Chairman Freedman: I think we need more meetings of this sort. We need more speakers like Dr. Steik. I think if nothing else has been portrayed this evening, and a good deal has been, this has: that the benefit to be derived from knowing one's subject intimately and knowing one's part just as intimately, is tremendous. I think, Dr. Steik, you are to be congratulated upon your most interesting exposition.

Dr. Steik: I hope that I left the impression at least that I think there is nothing perfect, that the oils, no matter what kind they are, have certain defects, more or less, and these defects might cause trouble sometimes. I wish you people who are applying and using these oils would not quickly jump at a conclusion and say, Well, white oil did that, or this oil did that. Before a priori blaming the oil, stop to think: there might be some other cause for the trouble than the oil.

ANNUAL MEETING NEWS

According to William J. Kelly, Jr., general chairman for the Annual Meeting in Chattanooga on December 6th and 7th, arrangements are going ahead rapidly in completion of plans. It is suggested that all members make hotel reservations as soon as possible. One hundred and ten rooms are already reserved at the Read House out of 200 rooms which are being held. The Hotel Patten, only two blocks away, has 200 rooms available.

After the banquet Saturday night a Textile Ball, floor show and style show will be held. The various textile manufacturers in the Chattanooga area will have displays and all the show windows in the down town district will feature fabrics made in this section and also the A.A.T.C.C. Convention.

ANALYTICAL METHODS
for a
TEXTILE LABORATORY

Our supply of copies of this publication by Walter M. Scott has been exhausted.

H. C. CHAPIN, Secretary

Proceedings of the American Association of Textile Chemists and Colorists

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—H. C. Chapin, Secretary, Lowell Textile Institute, Lowell, Mass.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive.

Note: Persons who have obtained employment should notify the secretary at once. Prospective employers may file vacancies either with the secretary or the American Dyestuff Reporter.

A-3

Education—Ph.B., Brown University, 1920. Two years post-graduate work at M.I.T.

Experience—2 years instructor at M.I.T. 2 years as research chemist in print works (Gum thickenings, application of dyes, dye testing and evaluation. 4 years as chief chemist in bleaching, mercerizing, dyeing and finishing plant. 4½ years as research and plant chemist in silk mills (Colorimetric work in color matching, dye testing and identification and testing of chemicals). 2 years as organic research chemist (laboratory and semi-plant research on organic chemicals, intermediates and dyestuffs). Age 35, married. Will go anywhere, references.

A-6

Education—Analytical Chemistry and Dyeing Course, Lowell Textile Evening School.

Experience—Seven years as print color and dye chemist in printing, dyeing and finishing plants; recently in charge of textile printing department of dyestuff manufacturer.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-4

Education—B.T.C. 1934, Lowell Textile Institute.

Experience—Assistant chemist in cotton knitting plant; second-hand in woolen knit goods dye house. Will go anywhere; references.

A-B-5

Education—Graduate of the University of Lausanne, Switzerland. Doctor's degree in Chemistry. Knowledge of French and German.

Experience—Eleven years with large bleaching, dyeing, printing and finishing plant as assistant Chemist and then Chemist in charge of the Laboratory. Experience in dyeing and printing cotton and rayon fabrics; research and analytical work. Woman.

A-B-6

Education—B.S. in chemistry, Cooper Institute.

Experience—Seven and one-half years in application laboratories of large dyestuff manufacturer. One year as plant chemist in dyehouse and print shop. Seven years as chief printing colorist on silk, rayon and cotton. 33 years old; married; will go anywhere; references.

A-B-C-2

Education—Graduate of Lewis Institute of Engineering of Chicago and graduate of Philadelphia Textile School (Chemistry and Dyeing department).

Experience—Has had extensive experience as assistant chemist and colorist in silk printing, dyeing and finishing; also dyeing raw stock wool; and dyeing and finishing cotton and rayon. Age 30; married; references.

A-B-C-3

Education—3 years at Brown University and Drexel Institute.

Experience—2½ years in dyestuff laboratory; 3 years as second-hand, dyeing indanthrene and direct colors on rayon skeins; 6 months as boss dyer on silk and cotton ribbons and hosiery; 3 years overseer of dyeing and finishing rayon tubing. Can handle laboratory, dyehouse, finishing or outside service. Age 30; married.

A-B-C-4

Education—Graduate, University of Michigan, in Chemical Engineering, 1930.

Experience—One year as assistant chemist and research engineer with metallic packing concern. Three years' experience dyeing and finishing rayon tubing, last two years being foreman dyer. Familiar with other kinds of dyeing. Working knowledge of Spanish. Age 28. Married. References.

A-B-E-F-I

Education:—Ph.D. in Chemistry, Pennyslvania, 1927; Graduate work in Chemical Engineering, M. I. T., 1918.

Experience:—Five years teaching, eleven years industrial and consulting experience on cellulose, synthetic fibers, dyes, textiles, oils and soaps. Now head of Chemistry and Dyeing Division of leading textile school. Age 45 years, married, member Alpha Chi Sigma and Tau Beta Pi, publications, references. Now on summer vacation.

A-C-1

Education—4 years at Newark Evening Technical School in Chemical Engineering.

Experience—8 years in manufacturing, research, testing of soaps, oils, gums and finishes and application of same in all phases of the textile industry. Age 23, single. References.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following: celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—Eight years as boss dyer on skeins and ribbons. Over ten years as chemist and head dyer for a large hosiery mill. Experienced on Silk, cotton, rayon and wool in skeins, ribbons, piece goods and all kinds of mixtures. Willing to go anywhere. Not afraid to work or face responsibility. Can handle help efficiently.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies' and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-9

Experience—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere.

B-12

Education—2 years days at N. Y. U. and 3 years nights studying chemical engineering.

Experience—1½ years asst. colorist, 5½ years colorist. Experienced on vats, commercial and fast colors on cotton and cotton-rayon mixtures. References; age 29; married.

B-13

Experience—Large experience as an assistant colorist chemist in silk printing, dyeing and finishing; also on cotton and wool dyeing. References.

B-14

Education—Rhode Island School of Design.

Experience—Familiar with all classes of wool dyeing. Seven years with large carpet mill as dyer and processor of washed oriental rugs. Will go anywhere, married, 37 years old. References.

B-15

Education—B.T.C., Lowell Textile Institute, 1934.

Experience—Experience in dye house running washers, dye kettles and as a dye weighter.

B-16

Education—Chemistry and Dyeing Dept., Philadelphia Textile School.

Experience—Head dyer and chemist on all types of hosiery; dyeing silk, cotton, Bemberg, rayon and unions of same; Celanese and immunized cotton effects. Age 27, married. Will go anywhere.

B-17

Education—Lowell Textile Institute (Chemistry and Dyeing Course) 1916; extension courses at Brown University.

Experience—6 months dyeing wool at finishing company; 2½ years research work on bleaching, dyeing and finishing at dye works; inspector of textile equipment, U. S. Ordnance Dept., during war; 15 years as superintendent of dyeing at finishing company, including all types of colors on cotton piece goods and some rayon and celanese; handled chemical work at last named plant for many years as well as dyeing. Age 40, married, prefers East. References.

AMERICAN
DYESTUFF
REPORTER

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ON GETTING ALONG WITH PEOPLE—V

(Continued from last issue)

More About Mill Experiments

IT is apparently true that leaders of men are successful because they have the knack or the art of getting other people to do what they want done. It is not easy to get far in any business position by one's own unaided efforts. Whether or not *they* know it, you can only succeed through the aid of other people—and this is particularly true in such work as directing experiments in a mill. You depend upon very much the same things as you read about in the "success" stories in the popular magazines. They are merely much less spectacular.

The superintendent or foreman is really an executive and frequently it is no longer his province to direct experimental work. However, if it is his hobby by reason of education or temperament to consider himself a great experimenter you will have to take that into account and to cater to it.

If the foreman is actively directing the work after it has been requested it is best to stay on the job and watch it through just the same as if you were doing it yourself. The most unbelievable and unexpected things can happen to experiments, or there may be unavoidable influences that are liable to be overlooked.

As an example of the last, piece goods or chains of yarn are liable to be run in the middle of a longer run of continuous production. Frequently while sewing or tying-in there is a delay while part of your sample is still in process. You should not only know that fact, but know how long it was delayed and what effect the delay had, if any. If one end of your sample stood on a dryer or in an ager for several times the normal length of time it might be quite misleading, if you were not there to see and mark that end, should you happen to take your samples from it for shade, fastness tests, or color of the white.

Avoiding such troubles is not likely to worry the workmen and may escape the thought of the foreman. You have to call attention to such things without appearing to try to tell them how to do their own work. The next truck of goods or the interrupted run should be right there to follow through without delay. A simple and sometimes better expedient is to tie on enough "leader" to carry your sample entirely through the machine in a normal length of time or to allow plenty of extra length to your sample.

In some kinds of work it is possible to guard against trouble by having automatic checks such as a series where each member differs from the next in some simple way so that an error will show up as "being out of line." Sometimes a check is provided and some other useful purpose served by running two or more kinds of goods in parallel experiments.

It is frequently best to check your own ideas, as well as the workmen in the mill in some such way as just described which is not conspicuous or obvious so that no one's feelings are ruffled. But, if you think the help are likely to be sloppy, or to make mistakes or in exceptional cases that someone might try to interfere with the success of the experiment, it is sometimes best to make a rather conspicuous display of care in checking up all details like temperature, Twaddle, time or whatever is concerned, as well as to stick right on the job.

It is usually best not to make superfluous suggestions or to call attention to minor faults. Attention should be called to anything that actually interferes with the purpose or success of the experiment, and you should carefully explain why if your idea seems to be questioned.

If a mistake is made learn something from it. I have frequently learned more from a mistake in running a sample than I would have if the experiment had gone as planned. However, this is not to be emphasized too much to the person making the error. The fault should be pointed out, good naturedly if possible, but clearly indicated as something wrong. Ordinarily it does not do any good, to bawl people out and make a big fuss. Save your own nerves and digestion, salvage what you can, and see that the thing goes right the next time.

Undoubtedly everyone will not agree with these mild instructions. Variation of experience in such matters leaves them largely a matter of opinion. You can't tell just how it would have worked out if you had done differently but it is undoubtedly best to try to get along as peaceably as possible.

The beginner may have some question on how to act with the help. Do not try obviously to be too chummy, or too aloof. Do what is most natural. I think it is well to try to help if you can do so without getting in the way. It is a good thing to learn how to handle yarn or cloth and how to run the machinery and it is a good thing to let some workman show you how.

Ask questions. Don't be afraid of showing what you don't know, especially if there is a chance that you will show it later, and perhaps to your greater disadvantage.

There are different ways of looking at this. I think it is best to get the essential information, but with reasonable care not to make a bad impression. Ask as though you want to confirm your own ideas on the subject.

To the contrary, however, in other cases I have learned all that I wanted or needed to know by just keeping quiet and noting what is said by others and what happens. In this way you do not display too much ignorance or appear to be unduly curious. Many times it is best to ask only for essential information and pick up the rest as you go along.

Ordinarily the person to ask is the one in direct charge of the department, usually the foreman. Do not go to the help for necessary information except in case of emergency, and verify it later with the foreman with due apology.

If a workman wants to talk, listen to him. You will frequently pick up little points of vital importance that are so obvious to the foreman that he may not think to mention them.

Above all, when asking questions do not make them sound critical. It is better to appear ignorant or to remain ignorant than to ask questions which sound like unfavorable criticism.

(*To be concluded in the next issue*)

● TRAINING SCHOOL

The Canadian Association of Textile Chemists and Colorists has been conducting, during the past week, in the Technical High School at Hamilton, Ontario, a training school for dyers and assistant dyers. The course consisted of a series of lectures designated to aid the practical man in his work in the mill. Each day was given over to the representatives of a particular company to deal exclusively with one type of fiber. Three sessions daily were held with lectures in the morning, afternoon and evening. The following was the program of instruction:

Monday, August 19—Wool—Consolidated Dyestuffs, Ltd.

Tuesday, August 20—Cotton—National Aniline & Chemical Co.

Wednesday, August 21—Silk—Geigy Co., Inc.

Thursday, August 22—Rayon—Ciba Company, Ltd.

Friday, August 23—Bleaching—Canadian Industries, Ltd.

A more complete report of this undertaking will appear in our issue of September 9th.

● BAST FIBER WEAKNESS

The Textile Foundation's valuable additions to existing knowledge of the physical properties of textile fibers are continued in the August number of *Textile Research*. G. Gordon Osborne, a Textile Foundation fellow who worked under the direction of Prof. E. R. Schwarz at M. I. T., continues his Observations on the Structure of Flax, Manila and Jute. One of his most important findings is that all bast fibers have the inherent structural weakness that he discovered in ramie; this being due to fissures in the cell wall. These fissures when complementary, or opposite, greatly reduce the fiber thickness at such points, thus resulting in tearing rupture at a lower load than straight tension, and also render the fiber weak to bending and flexure. Severe mechanical treatment tends to accentuate the number and depth of these fissures.

Another valuable contribution in this number is a report on the Degradation of Silk Fibroin by Acid and Alkali, by Eunice Walde and Rachel Edgar of the Dept. of Chemistry, Iowa State College. They find that alkaline degradation of silk fibroin tends to leave a residue poorer in nitrogen, and acid degradation a residue richer in nitrogen than the original fibroin. Alkaline degradation of wild silk fibroin leaves a residue richer in nitrogen than the original fibroin or the residue from acid degradation. The more rapid loss of tensile strength than of weight or nitrogen indicates that acid and alkali first bring about a general disintegration of fibrous structure without the formation of soluble products.

● CEROL TFS

Sandoz Chemical Works are announcing a new compound, Cerol TFS, which is recommended by them for waterproofing textiles in a water emulsion at any temperature, even the boil. It is thereby said to be possible to obtain better penetration on heavy fabrics which cannot be properly impregnated at low temperature.

Furthermore, Cerol TFS is said to be extraordinarily stable to a range of materials used for weighting or filling canvas goods and similar fabrics, such as waxes, starches, glue, gelatin, tallow, clays, talcum, and may be mixed with these in any proportions. Mildewproofing and mothproofing compounds may likewise be added. Thus, it is stated, the product often permits the complete wet finishing of fabrics in a single operation. By reason of the possibility of keeping the bath at the boil, complete penetration is claimed to be achieved and the water-repellency is claimed to be of a high order. It is further said that the material saving in time over the customary methods necessitating several baths contributes to render the use of Cerol TFS economical.

A sample book is available upon request which contains a number of practical formulas for various types of fabrics and swatches of different materials treated with this product.

● GENERAL RELEASE

General Dyestuff Corp. announces release of the following product. A copy of the bulletin describing this release may be obtained on request.

Fastusol Brown LGA—a yellowish brown said to be of superior fastness to light and with particularly good leveling properties.

Washington News Letter

By WALDON FAWCETT

UNEXPECTED prolongation of the Congressional session with the primary object of enacting tax legislation is not without its influences, both direct and indirect, upon legislation dealing with commerce and industrial property. An immediate consequence has been the advancement of certain measures which contact the dyestuffs industry. Specifically, the Copeland Bill for revision and extension of the Federal Food and Drug Act, and the Duffy Copyright Bill, to which amendments have been proposed to protect textile designs and other original designs. Indirectly, the forcing of the "must" program at the summer sitting of the national legislature may prove encouraging to proponents of all classes of special legislation, in that it should allow more time, in the Congressional session starting next January, for the consideration of projected additions or amendments to the statutes desired by technical, professional and business interests.

FILING AND INDEXING SERVICE FOR GOVERNMENT PUBLICATIONS

Illustrative of the constructive measures which find opportunity for attention when Congress is not overburdened with major issues is the Secrest Bill, reported favorably by the Committee on Library of the House of Representatives. This Bill (H. R. 4015) authorizes and directs the Secretary of the Interior (acting through the Office of Education) to devise a comprehensive filing and indexing service for useful government—both Federal and State—publications and to furnish such service to institutions and to the public.

It is a well known fact that many useful Government publications, which are produced at large initial cost, are wasted because no provision is made for their careful preservation in such manner that they are easily accessible to persons interested in the fields covered by the respective publications. The purpose of the proposed service is the conservation of all State and Federal publications, making them more useful by classifying, indexing and filing them in such manner that not only will the documents be well cared for but all publications on any one subject will be found in one quarter. The Acting Director of the Budget, in approving the principle of the proposal has suggested that possibly the present indexes prepared and distributed by the Superintendent of Documents might be amplified to serve the purpose of the proposed clearing house, thus making it unnecessary to set up another Government agency.

COTTON EXTENSION PROMOTERS ENCOURAGE COLOR TIE-UPS

Captains of the New-Uses-For-Cotton campaign of the U. S. Department of Agriculture, as a means of accomplishing their ends, are lending moral support to the movement which seeks to employ sympathetic color plans as a means of tying together different classes of textile products. The experience of this promotional bureau with the different dyes successively used on the duplex textile bag invented under its auspices has convinced the officials of the importance of color harmony as well as design conformity if a spirit of unison is to pervade textile products used in the same environment. In line with this spirit, the cotton expansionists are manifesting interest in all new cotton fabrics or fabric-applications. As, for instance, the lately-introduced cotton curtains, which, while adaptable to standard shade rollers, produce the effect of a Venetian blind.

RESEARCH ASSIGNMENTS AT NATIONAL BUREAU OF STANDARDS

A revised list, lately prepared, shows that fourteen organizations are, at the present time, accorded research associate privileges at the National Bureau of Standards. Of the forty-three specialists enrolled, eight are engaged upon research in textiles. The personnel is as follows: M. Harris and W. E. Emley, Jr., for the American Association of Textile Chemists and Colorists; G. Becker conducting the manila fiber research of the Cordage Institute; E. M. Schenke, H. E. Shearer and E. S. Benson, representing the National Association of Hosiery Manufacturers; and C. H. Hamlin and C. M. Roeder, engaged, in behalf of the Underwear Institute, upon a project concerned with standard sizes and measurements for underwear.

It is worthy of note that whereas the present roster of associated organizations shows a considerable shrinkage under the number and the diversification of the predepression muster, there has been an increase in the scope of the work on textiles. With the Underwear Institute replacing the Association of Knit Underwear Manufacturers of America, there have been no defections in the textile sector. Among the losses, however, has been the representation of the Munsell Research Laboratory which was engaged on colorimetry, and the withdrawal of the delegation from the National Association of Dyers and Cleaners which concentrated on general dyeing problems.

DESIGNERS AND COLOR PLANNERS RAISE AN ISSUE IN ETHICS

The past few months have witnessed the rise to controversial proportions of a debate on the proprieties of creative design service. The scene of this quarrel over ethics is the field of modern packaging. The basic prin-

ciple involved is, perhaps, translatable in some degree to every industry which makes use of original designs or combinations of colors. Independent, free-lance designers of containers, wrappings, etc., have taken umbrage at the policy of certain package supply houses and outfitters that are offering free service in desgining to customers who place orders for material with the design-donor. Professional designers who operate only on the basis of a retainer and service charge assert that the premium practice constitutes unfair competition in respect to artists whose livelihood is obtained by original designing and amounts to price cutting as against supply interests which do not give designs as a bonus. Giving edge to the duel of opinion is the accusation that, on occasion, proffers of free service in designing have been made to design-users who were already in negotiation with independent designers.

FRESH COMPLICATIONS IN COUNTRY-OF-ORIGIN MARKINGS

The Federal Trade Commission has been brought into the situation resultant from the more subtle efforts at evasion of the requirements for country-of-origin indicia on imports admitted to the United States. Heretofore the responsibility has been the straight-away obligation for nationalistic source-marking and has been handled by the Bureau of Customs of the Treasury Department. The new aspect, as represented by certain recent importations from Japan, has involved a double transgression. The country-of-origin legend has not only been printed in type so small as to be decipherable with difficulty under the best of conditions but had been so placed as to be totally obscured in any casual or normal inspection of the article. Specifically giving warrant to the Trade Commission to intervene was the appearance, in conspicuous place, on each article of the false declaration "Made in U. S. A."

In an effort to close a gap in the compulsory informative wall, officials of the Treasury Department have lately been vigilant in enforcement of amended regulations which require literal compliance with the requirement for country, not place, of origin. For one reason or another many foreign exporters in various countries had manifested a growing propensity to identify commodity birthplace by notation of province or unimportant city instead of country. The stiffened rules insist upon the conventional designation of the country rather than any political subdivision. Adjective forms are no longer acceptable. For example: "Sudan Produce" is rejected as insufficient, the requisite formula being: "Product of Anglo-Egyptian Sudan."

Textiles that cross international borders in course of processing must, as a rule, record the scene of dyeing and finishing. Thus, Chinese silk shipped to England and there dyed, printed and finished must be marked to show "England" or "Great Britain" as the country of origin. Linens woven in Ireland and printed in England are likewise required to specify "England" or "Great Britain," preferably the former.

NEW DIVISIONS OF U. S. FOOD AND DRUG ADMINISTRATION

The Color Laboratory at the U. S. Food and Drug Administration is unaffected by the latest expansion of the organization but the general effect of the move is in furtherance of specialization in chemical research. Two new divisions have been created, the urgency of the need therefore justifying deduction of funds for operation from income alloted for regulatory work.

To the new research unit known as the Vitamin Division is alloted the investigation of commercial products for which claims of vitamin potency are made. And the establishment of standards for this class of foods and drugs, which have increased in number so rapidly of late. To chemists, the very circumstance of the creation of this division is of general significance to the extent that it constitutes formal, official recognition of the fact that due allowance must be made, in planning chemical research, for explorative work which necessitates prolonged and painstaking tests.

Testing of the effects of new synthetic chemicals, used in foods and drugs is the first responsibility of the Pharmacological Division. With particular attention to the testing and standardization of the glandular preparations which have been introduced this past few years. In the larger aspect, the contribution of this new Division to the cause of progress in chemistry will, presumably, be found in the development of new methods for the identification and evaluation of new types of medicants—revelations that may be translated in degree to other branches of research chemistry.

TRADE PRACTICE CONFERENCE
New Model

Textile chemists and technicians have cause to show more than passing curiosity in the evolution of a new formula for the institution known as the Trade Practice Conference. The agency of voluntary cooperation for, or mutual subscription to, standard ethics of fair competition is the successor to the Code Authority of the NRA era. To evidence the extent of the contact with the textile community it is only necessary to recall that upward of one hundred of the now defunct NRA Codes bound the conformists to deference to rights of priority in designs, color plans, etc. Indeed, it will rest with whatever administrative machinery may be created via Trade Practice Conferences to provide the registration bureaus or clearing houses for original designs, colors, etc., which were contemplated under the Code Authority prospectus.

The Trade Practice Conference, in its original form, was a device of the Federal Trade Commission and was called into operation upon acceptance by not less than 85

per cent of the productive capacity of an industry. Under the new deal the instrumentality acquires added dignity and authority. For example, under the Nye-King Bill, pending in Congress, the Trade Practice Conference would have definite statutory basis. And, yet more important, the Trade Commission would have power to initiate a Conference on its own motion, instead of waiting upon the applications of industrial groups. Additional Governmental backing for the new model would also be the means of more conclusive determination whether a given industry was engaged in interstate commerce.

With upward of 200 industrial groups already moving for self-government, via the new pattern of Trade Practice Conference, it is evident that the new force must be reckoned with at all levels of production and distribution. As a further development of the ideal, there is the current movement on the part of scores of small industries, to consolidate their trade practice obligations through a "congress" of Conferences, conducted by a standing committee. Meanwhile the U. S. Department of Commerce has acted to meet the need for a directory of Code-Sponsoring Trade Associations. The muster roll shows that some 871 trade associations are so organized as to carry on under basic or subsidiary codes of fair competition. In this new Federal list there is indication, by keys, of the comparative size of all basic industries.

Acid Dyes—

(Continued from page 478)

Acid Dyes

The acid character of acid dyes is due to the presence of phenol groups, sulfonic acid groups, or carboxyl groups (COOH) within the molecules, which ionize in water to produce hydrogen ions. Monobasic acid dyes may be represented by the general formula HR, where H stands for the replaceable hydrogen of the acid and R the colored acid anion. Since acid dyes form true solutions in water, the ionization of HR may be represented by

$$HR \rightleftarrows H^+ + R^-$$

When salts are used in the dye bath, the effect is comparable to the behavior of inorganic acids when adsorbed in the presence of salts. That is, in the case of the acid dye the amount of the dye taken up by the adsorbent may be increased either by increasing the concentration of the anion (color ion) or the cation (hydrogen ion). On the other hand, the amount of acid dye adsorbed may be decreased by decreasing the concentration of either the color anion or hydrogen ion. Since acids are much cheaper than dyes, it is more economical to control the hydrogen-ion concentration of the dye bath, and thus regulate the amount of color anion taken up by the fiber.

Reference to the data show that increasing the hydrogen-ion concentration in the dye bath by the addition of hydrochloric acid increases the amount of dye taken up by the adsorbent.

Sodium sulfate, secondary sodium phosphate, and sodium tetraborate hydrolyze basic in aqueous solutions. Thomas and Baldwin[6] have shown that sodium sulfate decreases the hydrogen-ion concentration of acid solutions, and Kraus[2] has shown that a boiling solution of sodium sulfate reacts basic. Since these salts hydrolyze basic they will decrease the hydrogen-ion concentration of an acid dye bath and thus decrease the amount of acid dye taken up by the adsorbent. Furthermore, it will be observed from the data that the salts with the greater degree of basic hydrolysis have the greater restraining effect on the adsorption of acid dyes.

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● DYE PRODUCTION AND SALES

United States Production and Sales of Dyes by Classes of Application, 1934*

Class of Application	Production		Sales			
	Quantity	Percent of Total	Quantity	Percent of Total	Value	Percent of Total
	Pounds		Pounds			
Acid	11,635,651	13.35	10,481,882	12.43	$8,231,823	19.03
Basic	4,380,981	5.02	4,096,744	4.86	3,649,446	8.44
Direct	22,450,350	25.75	21,628,679	25.65	11,673,592	26.99
Lake and spirit-soluble ..	3,580,534	4.11	3,082,112	3.66	2,357,128	5.45
Mordant and chrome ..	4,154,390	4.77	3,397,155	4.03	1,636,925	3.78
Sulfur	13,441,952	15.42	14,215,259	16.86	3,142,387	7.27
Vats (including indigo) ...	26,963,234	30.93	26,846,964	31.84	11,996,370	27.74
(a) Indigo	15,818,492	18.15	16,120,738	19.12	2,887,320	6.68
(b) Other vats.	11,144,742	12.78	10,726,226	12.72	9,109,050	21.06
Unclassified.	570,520	.65	560,250	.67	562,944	1.30
Total	87,177,612	100.00	84,309,045	100.00	$43,250,615	100.00

*Figures from U. S. Tariff Commission.

● DYE EXPORTS

United States foreign trade in coal-tar colors, dyes, and stains was well maintained during the first half of the year with both imports and exports registering substantial value increases over the first half of 1934, according to C. C. Concannon, Chief of the Commerce Department's Chemical Division.

Exports of coal-tar colors, dyes, stains and color lakes reached 9,274,500 pounds valued at $3,164,685 during the first half of the year, compared with 10,270,600 pounds valued at $2,905,600 for the corresponding period of 1934, statistics show. American coal-tar dye exports enjoy wide distribution in world markets, Mr. Concannon stated, with China, Canada, Belgium, Mexico, Japan, and Brazil the outstanding outlets for such products. During June export shipments went forward to 49 foreign markets, according to preliminary figures.

Sponge—

Its Dyeing and Bleaching

By S. C. Calhoun

AMONGST the thousands of varieties of sponge animal found in the sea, only a few kinds are of use to man. The best qualities of sponge come from the Mediterranean Sea; typical varieties comprise the Fine Turkey Cup, the Fine Turkey Solid, the Hard Greek or Brown Turkey, the Elephant's Ear and the Honeycomb. Other kinds of sponge are obtained from the Bahamas, West Indies, Florida and Australian seas; for instance, the Glove Sponge, the Hard Head, the Hairy Yellow and the Fleece type are fished in the Florida and West Indies area.

The sponge is a sea animal of the Porfera class, the skeleton consisting of a substance termed spongin, this being a sclero-protein and resembling natural silk in chemical composition. When the sponge is first fished out, it is covered with a bluish-black skin, the interstices in the body of the animal being filled with an evil smelling milky fluid. The sponge is cleansed by squeezing, scraping and washing, after which it is carefully dried. Inferior kinds of sponge contain a fair percentage of sand and lime and are of a dingy color. To improve the appearance, the sponge is sometimes bleached by treatment with a dilute solution of hydrochloric acid, if the operation is carelessly performed, the sponge is tendered, with the result that it falls to pieces after very little use. Most people who have bought a cheap sponge will have noticed this fault.

Since the popularizing of colored bath sponges, dyers of these toilet requisites have been profitably employed, for even the cheapest grades are colored, if only for the sake of improved appearance. Ten or a dozen hues are wanted on sponge, most of the shades being pale ones. In a case where the sponge has a dingy color, it is necessary to bleach it before a pale, bright hue can be processed. There are one or two processes which may be used to bleach sponge, selection of a process being made in accordance with the condition of the commodity when it reaches the bleacher. Process 1. Steep the sponge for one one hour in a solution of soda ash, ½ deg. Tw. The liquor must not be heated to higher than lukewarm temperature. Wash the sponge well in warm water, then transfer to a bleaching bath containing 3 per cent of hyposulfite of soda and one part of commercial hydrochloric acid per six parts of water used in the bath. Process 2. Steep for one hour in a bath containing 1 part of commercial hydrochloric acid per six parts of water; wash well, then transfer to a cold bleaching bath containing 15 lbs. hydrochloric acid, commercial strength, and 20 lbs. hyposulfite of soda per 25 gals. of water used in the bath. Steep for one to two days. Another bleaching process consists of steeping the sponge in a cold solution of permanganate of potash until it assumes a medium brown color. The color is then discharged by treating the sponge in a solution of hyposulfite of soda and a little hydrochloric acid.

Sponge absorbs acid and substantive dyestuff with avidity, even at comparatively low temperatures. It is inadvisable to dye at the boil since this depreciates the sponge. On the other hand, if dyeing is conducted at too low a temperature, the color gradually loses depth through periodical soaping in use as a toilet requisite. Many acid and substantive dyes are well fixed by processing at temperatures between 45 and 65 deg. C. Two basic colors, Rhodamine and Victoria Blue, yield hues of satisfactory fastness to soaping at 50 deg. C. These are applied to sponge in a bath containing 1 to 3 per cent of acetic acid. They are used for pale rose and sky tints on bleached sponge. Almost any acid dyestuff of good fastness to soaping is suitable for processing sponge, the assistants used comprising acetic acid and Glauber's salt. Very little acetic acid will give good exhaustion, 2 per cent being usually found ample with most acid colors. From 5 to 10 per cent of Glauber's salt may be employed to act as a restrainer towards color absorption. Substantive dyes are applied in the same way as acid colors. Dyeing should be started in the cold, the acid being added in one or two lots after the sponge has become saturated with liquor. Chrome mordant colors are occasionally employed for fast shades on high grade sponge, since the color does not bleed no matter how drastically the sponge is soaped. Moreover, the color withstands treatment with alkali, followed by steeping in dilute hydrochloric acid, a procedure commonly adopted by laundry and dry cleaning concerns when renovating sponges which have become slimy after a period of use. When sponge is to be colored with chrome and alizarine dyestuff, the material is mordanted by overnight steeping in a cold bath at 9 deg. Tw. containing chrome alum; the next day, the stock is wrung and washed in cold water, then treated in a cold bath of sodium silicate, ¾ deg. Tw., for one-half hour, after which it is again washed thoroughly. The sponge is then ready for dyeing. A little acetic acid is generally used along with the chrome dyestuff. It is customary to impregnate the better qualities of sponge with a solution of glycerine in water after dyeing with the object of maintaining a supple condition in the sponge; material which has not been treated in this way becomes hard when dry and easily tears.

Diagrams of apparatus suitable for bleaching and dyeing sponge are depicted in Figs. 1, 2 and 3. In Fig. 1, a side-sectional view of a paddle-dyeing machine is shown, the four arms, R, of which gently agitate the charge of sponge during processing. The paddle rotates rather slowly, for a too rapid motion would be apt to damage the

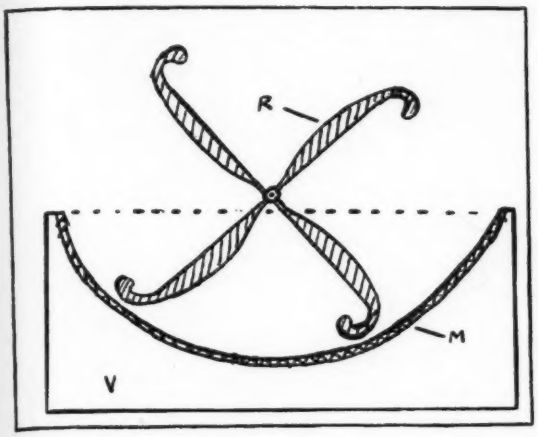

Fig. 1

sponge. The paddle arms are constructed of stainless metal, the outer end of each arm being furnished with a rounded boss which moves the sponge along the curved mesh bottom, M, without damaging the stock. Fig. 2 de-

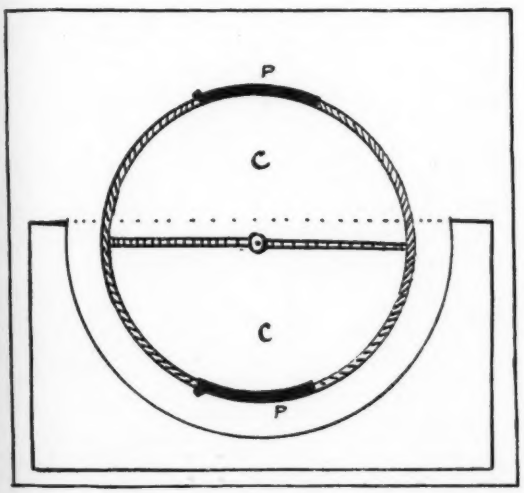

Fig. 2

picts an apparatus consisting of a revolving metal drum internally divided into two chambers for the reception of the sponge. Two parts, P, are provided for loading and unloading the stock. The ports are hinged at one side, the free side being fitted with screw clamps. The drum rotates in a shaped kettle fitted with water and live steam pipes. The diagram depicts an end view of the apparatus. In Fig. 3 is depicted a hand-operated piece of apparatus employed when bleaching sponge. A plunger, P, fits loosely in the barrel of the device; when the plunger rod, R, is depressed, the liquor is forced through the pack of sponge and thence into the cavity formed by the perforated false floor, a portion of the liquor ascending the pipe, F, and finding an outlet at the top of the barrel whence

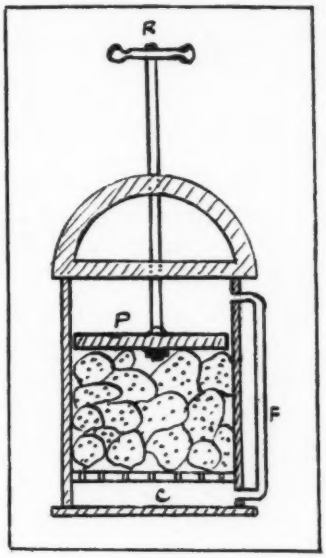

Fig. 3

it ultimately reaches the main bulk by way of the gap between the plunger and the barrel wall. When a batch of sponge is being processed in this apparatus, the plunger is only worked intermittently. A machine of this kind is useful for soaping sponge after it has been dyed, with the object of removing loose color from the interstices in the substance, for a certain amount of squeeze is essential in expelling the last traces of unabsorbed dyestuff.

Technical Notes

from Foreign Sources

The Truth Regarding Ostensible Defects in Dyeing Following Poor Mercerization

Batrevoy—TIBA 11, 187 (1933).—Some time ago, at Troyes (France), a certain strained relationship between the mercerizers and dyers arose, due to a series of complaints more numerous than usual. The chief complaint was based upon differences in color-tone between seams and the body of the hosiery concerned. The difficulty had seldom been noted as a ground of complaint, and the companies involved had recourse to investigations by the plant chemists in conjunction with experts from approved consulting laboratories. The discussions and reports of the investigators displayed a strange forgetfulness of the great responsibility of the spinner, and the author here calls attention to a number of points which should have been remembered in such cases of trouble with dyeing of mercerized cotton.

The success, he states, of the mercerizing process depends much more upon the proper spinning of the yarn than upon the process of mercerization. The mercerizer, in fact, is only an automaton, who mechanically treats yarns of all sorts of origins, without being able to correct the slightest defect in their manufacture. Mercerization, or, more exactly, the fabrication of mercerized yarn or weaves, does not succeed except when the spinner is always in contact with the mercerizer, or unless the latter appraises, that is, really, analyzes, the yarns before treating

them with caustic soda. If these conditions are not met, it is useless to hope for serious work or uniformly good results. The collaboration of the spinner with the mercerizer should be intimate and loyal, without which relationship no results whatever can be assured as satisfactory. If this collaboration is not possible—and this may frequently be the case, for most spinning plants do not mercerize, nor do most mercerizing plants spin their own yarn—a textile analytical laboratory ought to replace the liaison. Such a laboratory, however, would have to be perfectly installed and equipped, or its benefits will be illusory.

For hosiery, yarns are prepared by mixing (up to 50%) American cotton with Indian cotton. This latter sort, often different in color, is so selected as to mix well, as to aspect, with American cotton. And the spinner, for financial reasons, will "cut" this mixture with cardings. In addition, Indian cotton does not mercerize well, nor does American cotton permit a mercerization equal to that afforded by Egyptian cotton, which is the one variety most susceptible to a good mercerization, but which the spinner is not able to use in reasonable proportions because of its higher cost.

It would be absurd to state seriously and gravely (the fact is so obvious) that a mixture badly prepared, not homogeneous lot by lot, cannot provide, on spinning, a yarn of regular composition and of unvarying tinctorial affinity.

This is true both for the mercerization and the dyeing of the product. In the first case, each variety of cotton possesses its own characteristic affinity for the caustic soda. Then, further, in a non-homogeneous mixture, the yarn is not of regular physical characteristics; there exist variations in the twist, which are often intolerable. The degree of torsion is greater in the thinner parts of the yarn. Mercerization takes place more quickly and proceeds further upon the more loosely twisted than upon the parts of a harder twist. Homogeneity of structure means uniform mercerization and dyeing, and vice versa.

Another factor not to be overlooked is the singeing. If this is irregular, the yarn acquires an irregular luster; it becomes dull on the parts where there should be some fleeciness. It is to avoid this trouble that the spinners cut down the time of singeing for fine yarns, for which the operation is less necessary than for coarse yarns.

Still another factor to be considered is the possible influence of prolonged steaming, under pressure, of American cotton, in order to bring it more into the condition of the Egyptian variety. Alteration of structure may easily result through careless use of this process.

As to defects in the mercerizing process, dry mercerization has been greatly blamed for some troubles. The author states positively, from personal knowledge, that, if the yarn has been properly spun, the method works with perfect success and satisfaction; penetration is complete with the rather loose twists used for hosiery. The author states also that this method of mercerization is wholly penetrative in nature, and does not produce simply a superficial mercerization, and so by consequence a superficial dyeing, but goes to the very core of the yarn if properly carried out. As to trouble from the seams acquiring a different tone, in dyeing, from that of the body of the hose, he considers that it is not actually a difference in tone, but merely a difference in luster, the seams having been exposed to greater pressure and greater friction on the platens of the machinery than is the case with the flat of the goods. He maintains that, if the yarn is rightly mercerized (that is, all this with the understanding that the spinner has produced a uniform yarn which can be properly mercerized), the dyeing will have been so through-and-through in nature that this apparent difference in tone will no longer be apparent—i.e., the color-tone will be so rich and full, by thorough dyeing, that there will be evident only a slightly different luster on the seams, but no suggestion of difference in color-tone.

Anthraquinone-azine Dyestuffs (Vat)

German Patent No. 498,293 (*May* 21, 1930)—*I. G. Farben-Ind. A.-G.*—The substances forming the fundamentals of this procedure are halogenated N-dihydro-1-2-2'-1-anthraquinone-azines, which are heated with cuprous cyanide in inert solvents. For example, 3-3'-dibrom-N-dihydro-1-2-2'-1'-anthraquinone-azine yields a product which has exchanged its halogen for cyanogen groups. Its vat is blue; cotton is dyed a handsome green-blue (oxidized color).

One example is given.

Azo Dyeings (Naphthol AS Series)

German Patent No. 499,535 (*June* 7, 1930)—*I. G. Farben-Ind. A.-G.*—The second components in this procedure are the anilides of 2-hydroxy-3-naphthoic acid, or of beta-keto acids, padded as usual upon the cloth, and developed with a diazo bath of a 2-5-dimethyl-4-6-dihalogeno-aniline (a dihalogenated para-xylidine). The dyeings are faster to kiering than those from 2-5-dichloranilines, for example. The products can of course be produced in substance as pigments, or upon suitable substrata as lakes.

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